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Chemical recycle of polyester waste using novel zwitterionic catalysts

Wang, Lei

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Chemical Recycle of Polyester Waste using Novel Zwitterionic Catalysts

Lei Wang

Supervisor: Dr. John Holbrey

Second supervisor: Dr. Gosia Swadzba-Kwasny

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School of Chemistry and Chemical Engineering

Queen's University Belfast

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Abstract

Waste poly (ethylene terephthalate) (PET) from drink bottles was depolymerized using novel zwitterionic imidazolium-2-carboxylate salts as catalysts (or catalyst-precursors) in the presence of ethylene glycol via glycolysis to give *bis*(hydroxyethyl)terephthalate (BHET). The influence of reaction temperature, glycolysis time, ethylene glycol:PET ratios, and the amount of the zwitterionic imidazolium-2-carboxylate catalysts used on the conversion of PET, isolated yield of BHET, and the selectivity of BHET in the glycolysis of PET were investigated.

The results demonstrate that 1,3-dimethylimidazolium-2-carboxylate can be an effective basic catalyst for PET glycolysis, with PET depolymerization of up to 100% observed. BHET was isolated from the reaction mixture with yields of up to 61.0% under the optimum reaction conditions using 0.15 g catalyst to 1.0 g PET in the presence of 10.0 g ethylene glycol (0.15:1:10 mass ratio) at 185^{o}C in 1 h. This is the first time that 1,3-dialkyl-imidazolium-2-carboxylates have been reported to be catalysts for glycolysis of PET and, compared to 1,3-dialkylimidazolium acetate ionic liquids, were more effective as catalyst in the glycolysis. The purified monomer was characterized by the nuclear magnetic resonance (NMR), mass spectrometry, and high performance liquid chromatography (HPLC).

***Key words**:* Poly (ethylene terephthalate) (PET), bis (hydroxyethyl) terephthalate (BHET), glycolysis, carbene, zwitterionic catalyst, imidazolium-2-carboxylate (NHC-CO_2)

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List of abbreviations and symbols

Unit

^{o}C	Degree Celsius
%	Percentage
mol	Mole
g	Gram
eq	Equivalent
ml	Millilitre
wt	Weight percent
min	Minute
h	Hour
Pa	Pascal
MPa	Megapascal
rpm	Revolutions per minute
mbar	Millibar
mm	Millimetre
mg	Milligram
MHz	Megahertz
ppm	Part per million
cm^{-1}	Reciprocal centimeter
atm	Atmosphere

Chemical formula name/solvent abbreviations

PET	Poly (ethylene terephthalate)
TPA	Terephthalic acid
EG	Ethylene glycol
BHET	Bis (2-hydroxyethylterephthalate)
DMT	Dimethyl terephthalate
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
H_2SO_4	Sulfuric acid
THF	Tetrahydrofuran
NaH	Sodium hydride
DMSO	Dimethyl sulfoxide
D_2O	Deuterium oxide
$CDCl_3$	Deuterated chloroform
NHC	N-heterocyclic carbene
^tBuOK	Potassium tert- butoxide
KHMDS	potassium hexamethyldisilylazide

Others

NMR	Nuclear magnetic resonance
TGA	Thermogravimetric analysis
v/v	Volume/volume
GC	Gas chromatography
HPLC	High performance liquid chromatography

ES-MS	Electrospray mass spectrometry
FTIR	Fourier transform infrared spectroscopy

Chapter 1

Introduction

1.1 Background

Polyesters are engineering plastics that are extensively used in the world across a wide range of applications. Poly (ethylene terephthalate) (PET) (**Fig. 1.1**) is the most commonly used example of polymers belonging to the generic polyester family. It is a favorable packaging material with excellent tensile strength, chemical resistance, processability and thermal stability. Compared with other packaging polymers, PET also has good barriers properties towards moisture and oxygen.[1]

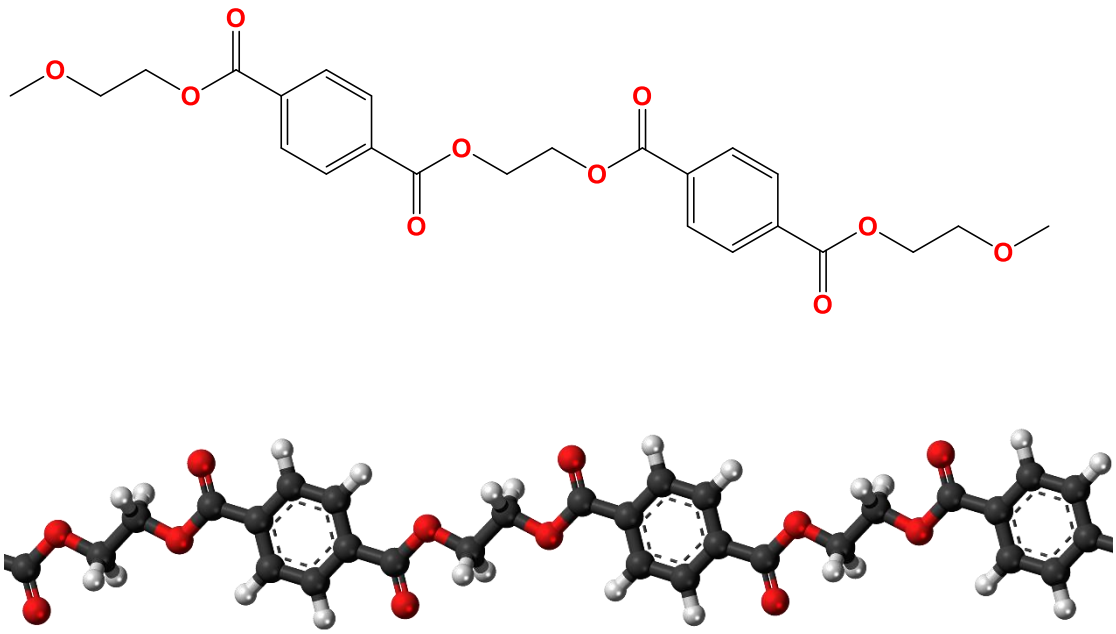


Fig. 1.1 The structure of poly (ethylene terephthalate) [PET].[2]

These chemical, thermal and materials properties have led to the use of PET as a packaging material. PET has become widely used as the major substitute for glass in the production of bottles, especially for use in packaging soft drinks and water, as well as general food packaging including 'direct to oven' trays for pre-cooked meals. A second major use of PET is in the production of synthetic fibres (polyester) used in clothing, furnishings, carpets, and fillings

owing to its excellent physical and chemical properties. The development of society raised consumers' demand for PET, accelerating the PET manufacturing process, and many global companies produced different PET.[3] For example, **Fig. 1.2** shows the global PET resin production capacity in 2017 which reached 30.3 million tons.[4]

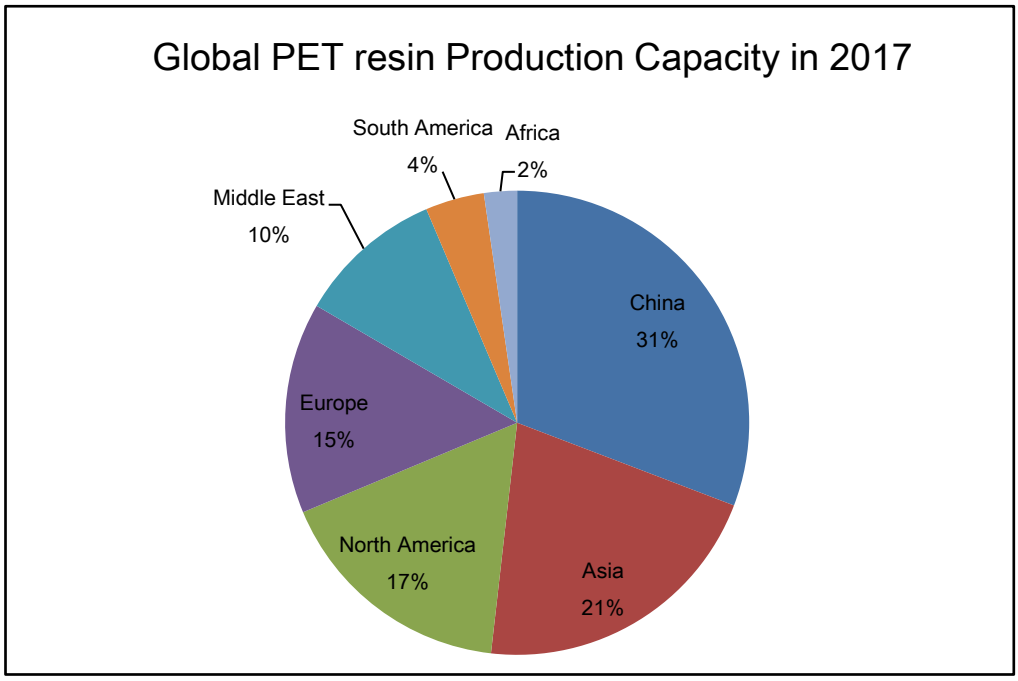


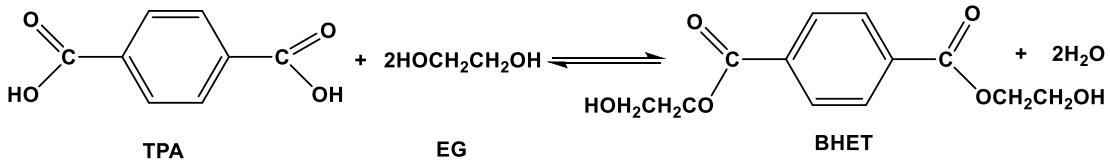
Fig. 1.2 Global PET resin production capacity in 2017.[4]

Despite PET having ester-linkages between monomer units, PET is non-degradable like most other synthetic (petrochemically derived) polymers which can generate an enormous amount of environmental pollution. The recycling of post-consumer PET packing materials was impossible because of the lack of knowledge about contamination of packaging polymers during first use or recollection.[5] Huge progress in PET recollection as well as recycling process in the last 20 years is due to the increasing trend of using plastic bottle and packages as a worldwide phenomenon. For example, according to the PET Resin Association, the U.S. recycling rate was about 31% in 2012, while it is

52% in the European Union. In 2016, the U.S. recycling rate had fallen below 29%. Nowadays, nearly 70% of all local authorities in the UK are now collecting pots, tubs, trays and other polymer wastes, resulting in approximately 155,000 tonnes per year.

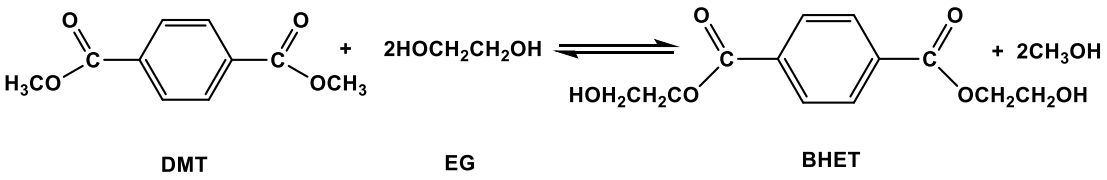
1.2 The Synthesis of PET

PET is formed through the esterification of terephthalic acid (TPA) by ethylene glycol (EG) or through the transesterification of dimethyl terephthalate (DMT) by ethylene glycol (EG).[6] **The Fig. 1.3(a)** shows the formation of the intermediate monomer *bis*(2-hydroxyethylterephthalate) (BHET) from the esterification of TPA. This esterification process is usually performed under mild pressure of 2.7-5.5 bar at temperatures between 220-260 ^{o}C where the sparing solubility of TPA can be overcome.[7] Water formed from the esterification reaction is continuously removed by distillation. **Fig. 1.3(b)** shows another route to formation of BHET from the transesterification of DMT. DMT and excess ethylene glycol are reacted at 150-200 ^{o}C in the presence of a basic catalyst. Methanol is removed by distillation and excess ethylene glycol is distilled off at high temperature.[7] Because of the increasing production of TPA and the reduced production of DMT at an industrial scale , the esterification from TPA to BHET has been a major process replacing the transesterification from DMT to BHET in the last years.



TPA EG BHET

(a)



(b)

Fig. 1.3 Formation of intermediate monomer BHET.[8]

Polycondensation of BHET to produce PET is shown in **Fig. 1.4**. In this process, the esterification or transesterification product BHET monomer, as intermediate or prepolymer in an excess of ethylene glycol as a solvent to generate higher molecular mass PET at the temperature of 270-280 ^{o}C under vacuum with the pressure less than 1 mbar. Like the esterification or transesterification reaction, the polycondensation reaction must be accelerated by catalysts. The produced PET in this process can be applied to making fibers or recording tapes.[6]

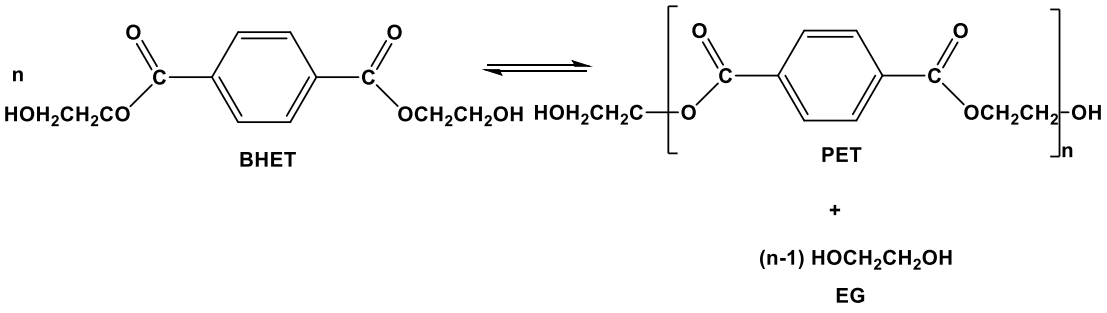


Fig. 1.4 Polycondensation of BHET to PET.[6]

1.3 Recycling of PET

The worldwide application of PET has caused large amount of PET waste. PET

is considered as a poisonous material owing to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents.[9] Governments and the general population are becoming increasingly aware of the serious environmental and economic problems with the increasing amount of PET wastes. It has accelerated the process of recycling PET waste. There are many ways of recycling PET waste including physical methods and chemical ones shown in **Fig. 1.5**.

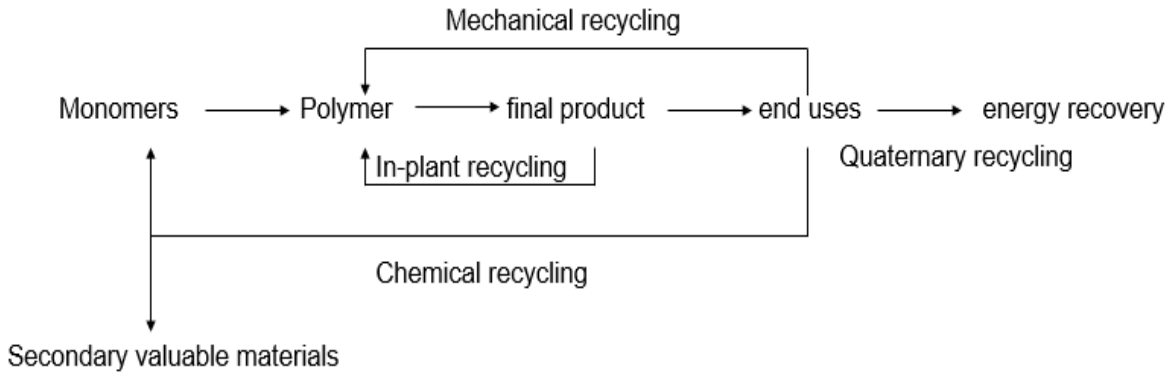


Fig. 1.5 Recycling techniques of PET.[10]

In **Fig. 1.5**, in-plant recycling, also as known primary recycling where the scrap materials that have similar features are recycled to original products, is the most established method for reusing polymer due to its simplicity and low cost. An example of in-plant recycling is the injection moulding of out of specification LDPF crates.[11] currently, most of the plastic solid wastes are recycled via this primary recycling.[12] However, the required clean, uncontaminated and single-type wastes limited the development of this method.[12] Mechanical recycling is the secondary recycling, which involves a number of treatments and operations: sorting and separation of wastes by resin, removal of dirt and contaminants by washing, plastic particle size reduction by grinding and crushing, extrusion by heat and reforming new plastic goods.[13] In mechanical

recycling process, polymer wastes such as PET bottles are collected, compressed and packed to transport to recycling plants where wastes are selected to remove impurities and then shredded, cleaned, and separated, and the remaining wastes turned into flakes and pellets which are recycled to reprocess in textile and sheet-making plants. A number of products found in our daily life are all from mechanical recycling processes such as pipes, window and door profiles, grocery bags, and gutters, etc. Compared with chemical recycling, there are a lot of advantages in the mechanical recycling, such as its simplicity of process, low cost, easy operation of available equipment, flexibility of raw materials supplies and little experimental pollution. However, the reduction of the molecular weight or intrinsic viscosity by thermal and hydrolytic degradation which is the major disadvantage of mechanical recycling influences the development of this method.[6] The tertiary recycling is chemical recycling which completes the transformation of the PET chain leading to the total depolymerization from PET to the monomer BHET, or partial depolymerization to oligomers or other chemical substances.[5] In chemical recycling, the formed product monomer BHET or other oligomers can be subsequently repolymerized to regenerate other polymers. Because PET is a polymer with functional ester groups, it can be cleaved by some reagents such as alcohol, water, acid, amine, and glycol. Thus，there are some methods in chemical recycling of PET including hydrolysis, methanolysis, glycolysis, aminolysis and ammonolysis. Energy recovery as well as the quaternary recycling refers to the recovery of the plastics' energy.[10]

In summary, various recycling technologies of PET have been presented in some papers, which have contributed greatly to PET recycling, treatment and recovery. Certain disadvantages such as the reduction of molecular weight or the contamination of raw materials appear when in-plant recycling and mechanical recycling are chosen as routes of recycling. Reusing and

decreasing single-life polymer materials are still major issues. Among the various methods of PET recycling, only chemical recycling conforms to the principles of sustainable development because it leads to the formation of the raw materials from which PET is originally made,[14] so PET decomposition and its conversion into reusable chemical products become one of the important recycling strategies for this material.

1.3.1 Chemical recycling of PET

Overall, PET does not decompose readily in nature although a few enzymes can degrade PET very slowly. With the use of PET and increase of PET wastes, chemical recycling of PET has become the best method to reuse the feedstock after comparing with other methods such as in-plant recycling, mechanical recycling and quaternary recycling which are illustrated in **Fig. 1.5**.

1.3.1.1 Hydrolysis

Hydrolysis can achieve the total depolymerization from PET to its monomers (TPA and EG) by water in an acid, alkaline or neutral environment under high temperature (200-250 ^{o}C) and high pressure (1.4-2 MPa) with a long depolymerization time. The process of hydrolysis can be performed as alkaline hydrolysis, acid hydrolysis and neutral hydrolysis.

Alkaline hydrolysis is usually carried out with the use of an aqueous solution of NaOH or KOH of a concentration of 4-20 wt%.[9, 15] Pitat et al.[16] have pointed that the alkaline hydrolysis of PET was advised by the use of 18 wt% solution of NaOH. In addition to the aqueous hydrolysis of PET, Oku et al.[17] have presented alkali decomposition in non-aqueous solutions such as dioxane or tetrahydrofuran as a mixed solvent with an alcohol which can accelerate the chemical degradation of PET. Alkaline hydrolysis of PET is shown in **Fig. 1.6**. In this process, EG and the disodium terephthalate salt (TPA-Na_2) are formed

in the first step, and then the mixture is heated up to 340 °C to evaporate and recover EG by distillation until pure TPA obtained. PET alkaline hydrolysis is widely used in the polyester fiber industry, especially in treatment processes of the fiber mechanical properties.[18] However, the need of high temperatures and high pressures as well as the long digestion times required and the trouble of regenerating the TPA monomer have limited the development of this method.

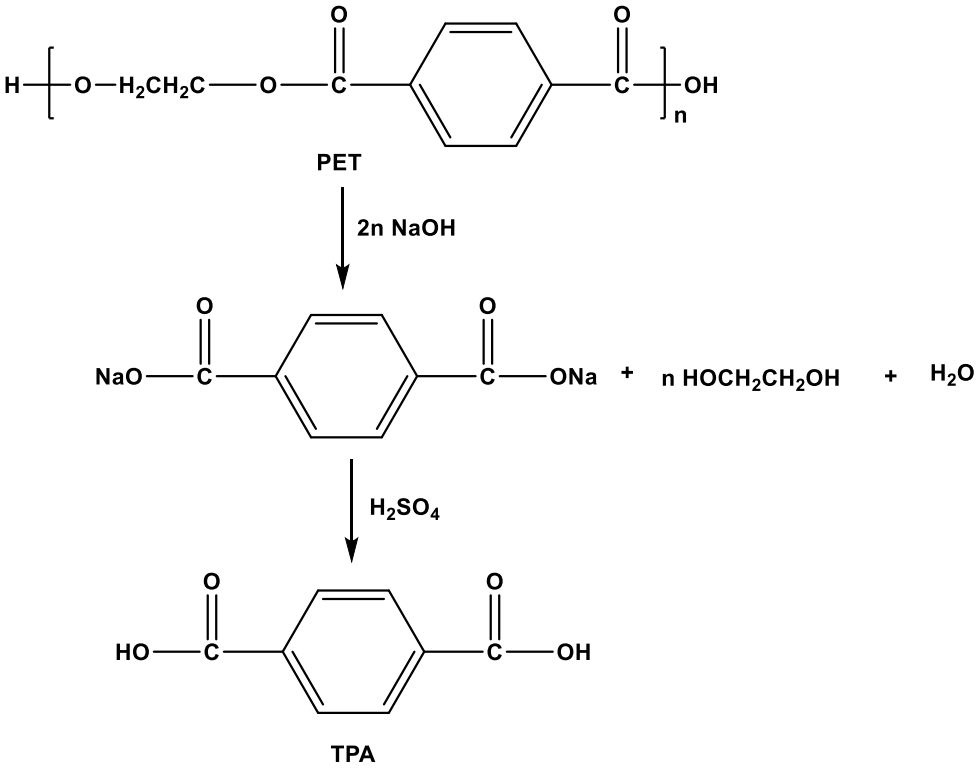


Fig. 1.6 Alkaline hydrolysis of PET.

Acid hydrolysis is carried out by using concentrated sulfuric acid to generate TPA directly as shown in **Fig. 1.7**. Yoshioka et al.[19] proposed an acid hydrolysis of waste PET powder using relatively dilute acid conditions and the reuse of the sulfuric acid by recovery methods such as dialysis. Achilias et al.[20] reported acid hydrolysis of PET in sulfuric acid at different temperatures and solution concentrations. However, the main disadvantage of acid hydrolysis is the high

corrosiveness and the generation of large quantities of inorganic salts and aqueous wastes by using concentrated sulfuric acid and the requirements of long reaction time and high temperature.

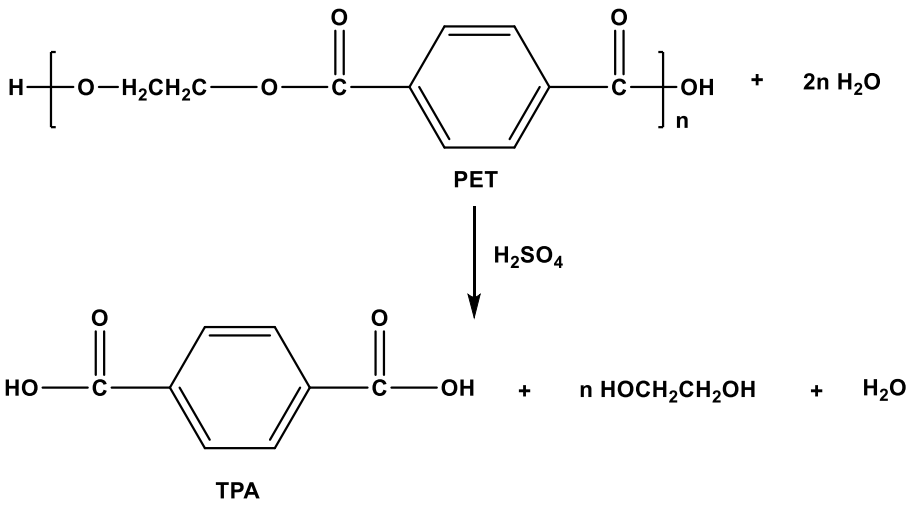


Fig. 1.7 Acid hydrolysis of PET.

In the case of neutral hydrolysis, the use of hot water or steam, high pressure (1-4 MPa) and high temperature (200-300 ^{o}C) in high-pressure autoclave conditions are required. Sato et al.[21] investigated the depolymerization of PET to TPA and EG in water at temperatures above 250 ^{o}C with the objective of enabling monomer recycling with 90% yield of TPA. To achieve this, the reaction temperatures had to be increased to 420 ^{o}C. Compared with both acid and alkaline hydrolysis, neutral hydrolysis can be considered as more environmentally friendly since it avoids the formation of substantial amounts of inorganic salts which are difficult to dispose of and a growing interest in this Technology is expected.

1.3.1.2 Methanolysis

The methanolysis process is degradation of PET through transesterification

with methanol at high temperature and high pressure, typically using zinc acetate, magnesium acetate, cobalt acetate and lead dioxide as transesterification catalysts to obtain dimethyl terephthalate (DMT) and EG as products (**Fig. 1.8**).

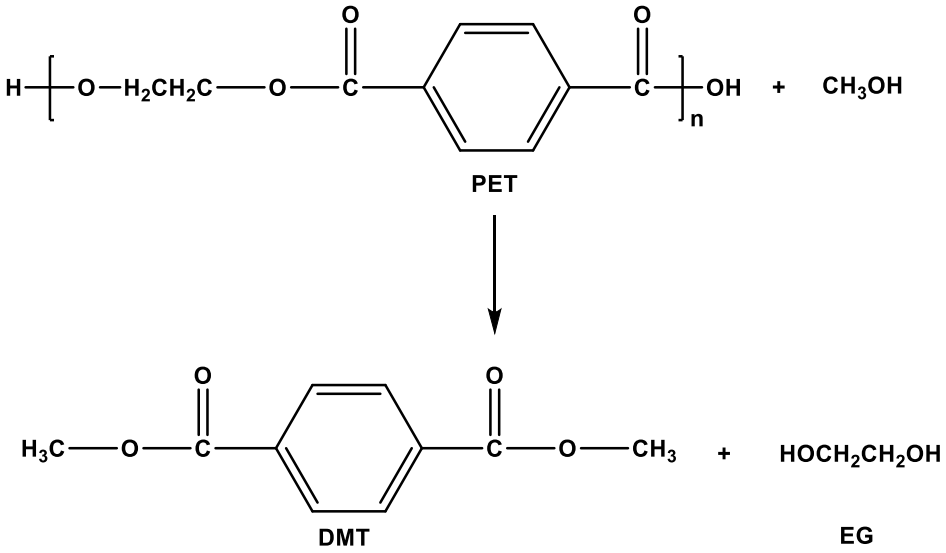


Fig. 1.8 Methanolysis process of PET.

Methods for the methanolysis have similar basic parameters, for example, Yang et al.[22] studied the methanolytic depolymerization of PET across a range of conditions and concluded that the optimal depolymerization conditions are temperature of 260-270 ^{o}C at a pressure of 9.0-11.0 MPa using a mass ratio of methanol to PET from 6-8:1. The aromatic product from methanolysis, DMT, is much easier to purify than BHET, and other products such as methanol and ethylene glycol are simply recovered and recycled.[23] However, there are associated high processing costs due to intolerance of the methanolysis, chemistry to feedstock contamination, and the need to subsequently convert DMT to TPA as direct polymerization of DMT to PET is no longer practiced as a commercial scale and all current production is from TPA. Nowadays, this process is utilized in the polymer generation line where waste PET emerging

in the generation cycle is used and monomers recycled are used as a part of the manufactured by polymer.

1.3.1.3 Aminolysis and Ammonolysis

Deep aminolysis of PET can be used to obtain the corresponding diamides of TPA along with EG (**Fig. 1.9**). The reaction was usually carried out using aqueous primary amine solutions such as methylamine, ethylamine, and ethanolamine at much milder temperature than those required for hydrolysis and methanolysis described above, typically using a temperature range between 20-100 ^{o}C to form bis(2-hydroxyethyl) terephthalamide (BHETA).[24] However, aminolysis process has been rarely used as a technique for PET recycling due to the profound polymer debasement.

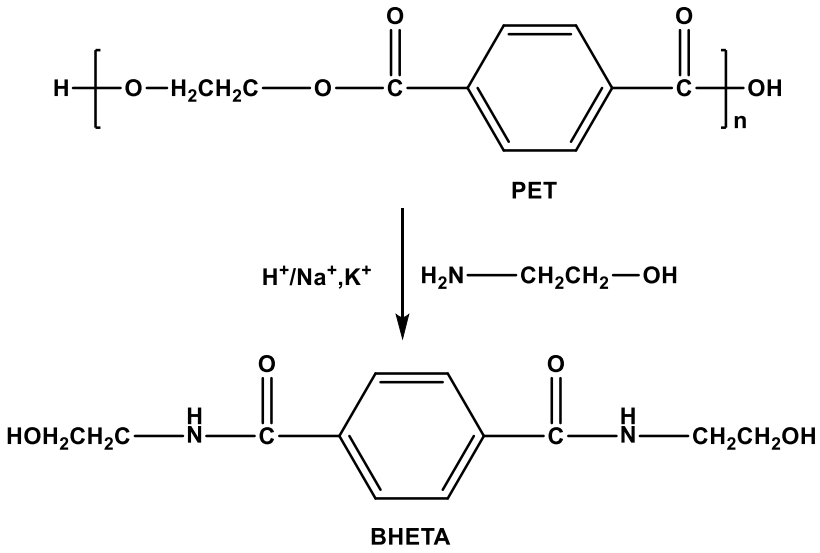


Fig. 1.9 Aminolysis of PET.

Ammonolysis is the reaction of anhydrous ammonia with PET to produce a terephthaldiamide (**Fig. 1.10**) which can be converted into terephthalic acid nitrile and further to p-xylylenediamine or 1,4-bis(aminoethyl)cyclohexane.[25] Ammonolyis of PET waste can be utilized well in postconsumer bottles under

a pressure of about 2 MPa in a temperature range of 120-180 ^{o}C for 1-7 h.

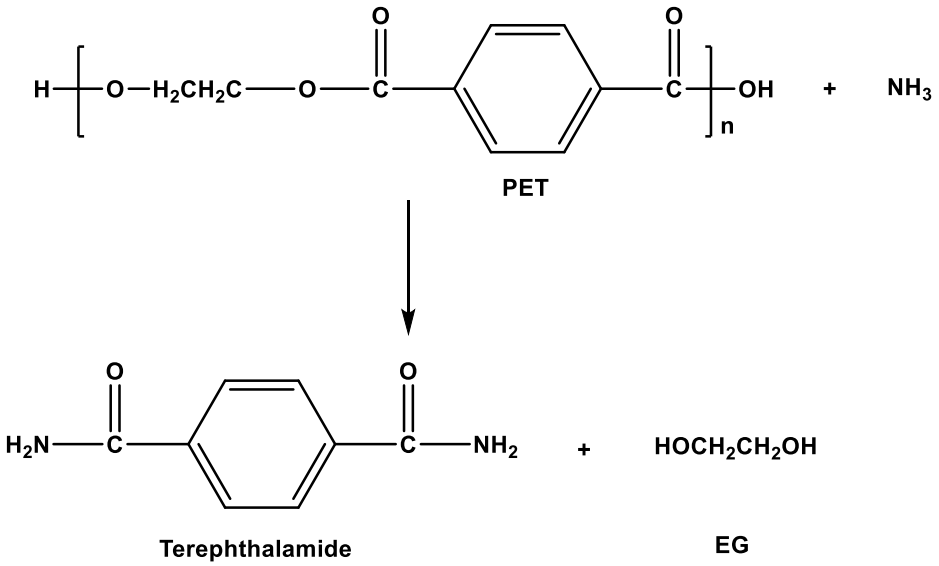


Fig. 1.10 Ammonolysis of PET.

1.3.1.4 Glycolysis

Glycolysis is the strategy for chemical recycling of PET which is currently attracting the most attention. This method can be used on a commercial scale with flexibility and the process has only minimal complexity. Moreover, with the current shift in PET manufacture from using DMT to almost exclusively TPA as the starting monomer, chemical recycling to bis(hydroxyethyl)terephthalate (BHET), the first intermediate stage in co-polymerization of TPA with EG, directly aligns recycling efforts with the commercial PET production processes in operation.

In the presence of ethylene glycol, PET is depolymerized through transesterification reactions with EG primarily forming BHET. Diethylene glycol,[26] triethylene glycol,[27]propylene glycol,[28] and dipropylene glycol[26c, 29] have also been used as solvents in glycolysis of PET as well. The glycolysis process is conducted across a wide temperature range between 180-250 ^{o}C

with reaction time between 0.5-8 h in the presence of a catalysts.[28b, 30] In this process, the effect of the reaction factors such as reaction temperature, glycolysis time, the amount of ethylene glycol and catalyst on the conversion of PET, the yield of BHET, and the selectivity of BHET have been investigated.

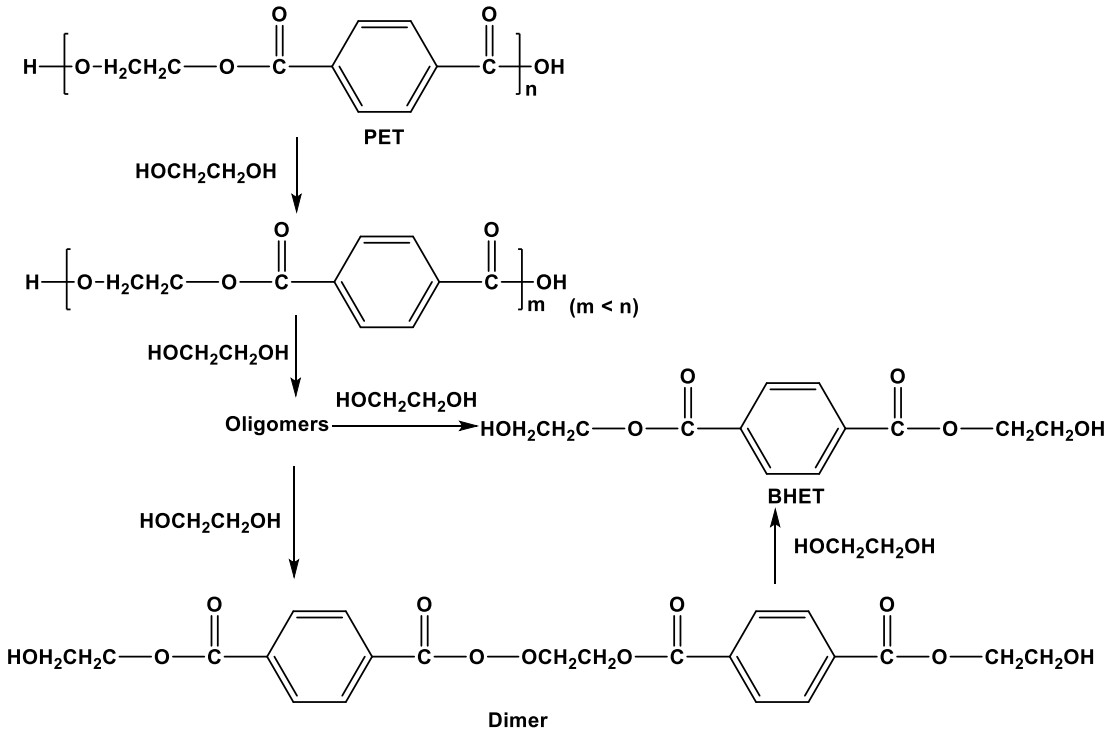


Fig. 1.11 Reaction pathway of glycolysis of PET.[31]

Fig. 1.11 shows the reaction pathway of glycolysis of PET which is first depolymerized into lower molecular weight PET oligomers with reduced degree of polymerization (m) from original PET (n) in the presence of ethylene glycol. With extended reaction times, the lower length PET polymers are further glycolyzed generating lower molecular weight oligomers and then to dimers and finally the monomer BHET.[31] Water is removed during the reaction to ensure that competing hydrolysis reactions are prevented. Expanding the rate and yield of BHET monomer, improving the glycolysis reaction conditions such as temperature, time, PET/EG proportion has become an important part

in the research of glycolysis of PET. The rate of glycolysis, and efficiencies of the reactions are highest when a catalyst is used. Many catalysts have been investigated, each of them having its own performance under different conditions which have been studied in many reports described below.

1.4 Catalysts of glycolysis

Studies on the kinetics of PET glycolysis have shown that without a catalyst the glycolysis process was so slow that complete depolymerization from PET to BHET monomer is not achieved.[32] Metal salts[33] have been predominantly studied as PET glycolysis catalysts, and recently ionic liquids have also been examined, with two distinct approaches incorporating either metallate anions[34] or basic anions[35] that could induce N-heterocyclic carbene (NHC) formation. NHCs have also been used under extremely mild conditions for PET glycolysis[36] in the laboratory, but require stringently anhydrous conditions that are not practical to scale-up.

1.4.1 Metal salts

Metal salts have an important role as catalysts in PET glycolysis. The use of metal salts including metal Co, Pb, Zn and Mn acetates, Zn, Li, Mg and Fe chlorides, Na and K sulphate, sodium carbonate and titanium phosphate as transesterification catalysts for PET glycolysis, and methanolysis have been reported. Metal acetates were the earliest group of metal salts investigated for the glycolysis of PET. Vaidya et al.[33] first used zinc acetate as catalyst for the polyesterification of the glycolyzed PET waste. In 1989, Baliga et al.[30d] tested and compared lead, zinc, cobalt, and manganese acetates as catalyst in the glycolysis of PET and found that zinc acetate was the best in terms of the extent of depolymerization and amount of monomer formed, with the overall catalytic activity order Zn^{2+} > Mn^{2+} > Co^{2+} > Pb^{2+}. At the same time, they

observed that when the reaction time was greater than 8 h, an equilibrium was obtained between BHET and dimer. Ghaemy et al.[37] in 2005 verified the reasonability of these four metal acetates catalytic activity order. However, Chen et al.[32b] in 1999 presented that an equilibrium state between the monomer and dimer was attained after only 2 h of reaction with zinc acetate as catalyst, in contrast to the 8 h reported previously by Baliga in 1989. Meanwhile, they found that the catalyst concentration facilitated equilibrium and increased the glycolysis rate.

In addition, the effects of different conditions such as reaction temperature, glycolysis time, EG dosage and the amount of catalyst on the yield of BHET, and the conversion of PET have been extensively studied using different metal salts as catalysts. For example, in 2005, Xi et al.[38] reported optimal conditions using zinc acetate as a transesterification catalyst of 196 °C, with reaction time of 3 h, at a mass ratio of EG to PET of 5:1, where catalyst loadings of 1 wt% (relative to PET) gave a BHET yield of 85.6%. Goje et al.[39] studied chemical kinetics, simulation, and the thermodynamics of glycolytic depolymerization of PET with metal salts catalysts to obtain monomeric products (EG and DMT) and presented optimal PET depolymerization conditions at 197 °C for 90 min and with PET partial size of 127.5 μm. Troev et al.[40] synthesized a novel catalyst titanium (IV) phosphate and compared it with traditional catalyst zinc acetate in the glycolysis. They reported that BHET yield of 97.5% could be obtained for glycolysis with EG at 200 °C over 150 min using 0.3 wt% catalyst: PET compared to 62.8% yield of BHET using zinc acetate under the same reaction conditions.

Zinc acetate is a highly active catalyst for the glycolysis, however, it is a heavy metal that can have a negative effect on the environment in high concentrations. Thus, more eco-friendly salts as alternative metal salts catalysts were investigated. For example, López-Fonseca et al.[41] studied the

effects of different catalysts including sodium carbonate, sodium decarbonate, sodium sulphate and potassium sulphate compared with zinc acetate on PET glycolysis and reported that comparably high yields of BHET were obtained using 1 mol% sodium carbonate and zinc acetate as depolymerization catalysts at 196 ^{o}C with an excess of EG. Although the activity of zinc acetate was significantly higher than that of sodium carbonate[32c] and zinc acetate is frequently used as catalyst for PET glycolysis, sodium carbonate was effective, and is an eco-friendly alternative which could address the negative environmental impact related to the toxicity and non-biodegradability of zinc. The use of metal catalysts can increase significantly the rate of PET glycolysis. However, their drawbacks also raise concern such as non-biodegradability and toxic nature of heavy metal (Zn, Fe, Mn and Co), low selectivity of the reaction towards BHET avoiding the formation of higher oligomers. So, it is especially crucial to search alternative, eco-friendly active salts as catalysts for the reaction.

1.4.2 Ionic liquids

Ionic liquids are salts that are liquids at low temperature (<100 ^{o}C) which represent a new class of solvents with nonmolecular, ionic character.[42] Ionic liquids have been studied and developed since the 1970s. However, ionic liquids are not new, for example, the first ionic liquid [$EtNH_3$] [NO_3] with a melting point of 12 ^{o}C was described by Walden in 1914.[43] With a lot of experiments, the melting points of ionic liquids have been reduced from high temperature (molten salts) to low temperatures which have made these fluids available for use in synthetic chemistry. Room temperature ionic liquid has been developed in the last forty years. In 1997, Seddon[44] proposed that room-temperature ionic liquids can be used as solvent for clean synthesis and catalysis processes due to low volatility, high thermal stability, high solubility,

low cost, and simplicity. In 1999, Welton[45] reviewed the preparation of room-temperature ionic liquids and the application of room-temperature ionic liquids as solvents for synthesis and catalysis. Similarly, Holbrey and Seddon[46] in 1999 described many of the catalytic processes which mostly had been taken through in industrial processes when using low temperature ionic liquid as reaction media such as the Dimersol/Difasol process, oligomerization of butene, Ziegler-Natta polymerisation, hydrodimerization of dienes, alkylation of olefins, Diels-Alder reactions, reduction of aromatic rings, and synthesis of linear alkylbenzenes. Since then, ionic liquids research has become popular with studies to replace volatile organic solvents or catalysts with their low flammability, electrochemical stability, high thermal stability, and low volatility.[47] Imidazolium heterocycles are popular cations in ionic liquid because their aromaticity makes them relatively stable and allows modification of the properties of ionic liquid materials by small variation in the substitution on the imidazolium cation. The most intensively studied imidazolium ionic liquids contain the cations 1-ethyl-3-methylimidazolium $[C_2mim]^+$ or 1-butyl-3-methylimidazolium $[C_4mim]^+$ as they are simple to produce, are relatively low cost, and can lead to ionic liquids with good physical and chemical characteristics such as low melting points and viscosities.[48]

Ionic liquids have only relatively recently been investigated as solvents and/or catalysts for glycolysis. In 2009, Wang et al.[35] first explored the dissolution of PET in a range of ionic liquids with $[C_4mim]^+$ cations and chloride, bromide, acetate, tetrafluoroborate, hexafluorophosphate and chloroaluminate(III) anions. They reported solubility, with polymer degradation, of PET in all the ionic liquids at 180 ^oC, except with $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$, and the ionic liquids could be used as solvents and catalysts to promote degradation of PET under relatively lower pressure and temperature and separate the products from the ionic liquid by the addition of water and filtration to reuse the

ionic liquid in further reactions.

It could be concluded from this first study that PET dissolution and degradation was induced through hydrolysis with water present, or added, to the ionic liquid. Liu et al.[49] in 2009 also explicitly studied the hydrolysis of PET using ionic liquid 1-n-butyl-3-methylimidazolium chloride ([C_4mim][Cl]) as solvent and the acid-functionalized ionic liquid 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([HSO_3-pmim][HSO_4]) as a catalyst and reported almost 100% PET conversion and > 88% TPA yield.

Following on from these first studies, basic and acidic ionic liquids have been studied for glycolysis of PET. In 2011, Yue et al.[50] examined the use of 1-butyl-3-methylimidazolium hydroxide ([C_4mim]OH) as a basic ionic liquid catalyst, reporting higher catalytic efficiency in the glycolysis of PET compared with 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, and 1-butyl-3-methylimidazolium bicarbonate, with 100% PET conversion and 71.2% BHET yield under the optimum conditions with a reaction temperature of 190 ^oC, time 2 h, 5 wt% [C_4mim]OH, and the mass ratio of PET:EG of 1:10. In addition to basic ionic liquids, some metal-containing ionic liquids (acidic ionic liquid) were also studied in the degradation of PET. In 2013, Wang et al.[34] synthesized different 1-alkyl-3-methylimidazolium halometallate ionic liquid by mixing crystalline powder of [amim]Cl with $MnCl_2$, $FeCl_3$, $CoCl_3$, $CuCl_2$, and $ZnCl_2$ and used these ionic liquids as catalyst into the glycolysis reaction; Finally, they found that using [amim][$CoCl_3$] and [amim][$ZnCl_3$] as catalysts, the PET conversion and BHET selectivity were both higher under mild conditions than traditional ionic liquids catalysts; Especially, when using [amim][$ZnCl_3$] as catalyst, the conversion of PET and the selectivity of BHET were attained up to 100% and 81.0%, respectively, at 175 ^oC in 1.25 h which was higher than that catalyzed by [C_4mim]OH, [C_4mim]Cl, [C_4mim]Br, [C_4mim][HSO_4], [C_4mim][$FeCl_4$]. Based on [amim][$ZnCl_3$], Yue et al.[51] in 2013 described the

synthesis of $[C_4mim]ZnCl_3$ and presented that the PET conversion and the BHET yield were achieved at 100% and 83.8% with low loading catalyst at 0.16 wt% when using the $[C_4mim]ZnCl_3$ as catalyst which can be reused up to five times. In 2014, they[52] compared $[C_4mim]ZnCl_3$ with other metal-containing ionic liquids $[C_4mim]MnCl_3$, $[C_4mim]PbCl_3$, $[C_4mim]FeCl_4$, $[C_4mim]NiCl_3$, $[C_4mim]SnCl_3$, $[C_4mim]AlCl_4$, and $[C_4mim]CuCl_3$ and concluded that $[C_4mim]ZnCl_3$ was the most effective catalyst to achieve highest conversion of PET and yield of BHET at 180 ^oC for 5 h. In 2015, Wang et al.[53] reported that $[C_4mim]_2[CoCl_4]$ can achieve 100% PET conversion, and 95.7% mass fraction of BHET in products under the optimum conditions at 175 ^oC for only 1.5 h. However, in common with catalysts such as zinc acetate etc, these ionic liquids still incorporate heavy metal ions.

Comparing with traditional ionic liquids as catalyst in the glycolysis, Al-Sabagh et al.[54] in 2014 first presented a detailed study using the acetate-based ionic liquid $[C_4mim][OAc]$ as a catalyst for PET glycolysis, which was also reported as an efficient catalyst in the methanolysis[55] and hydrolysis[56] of PET; The effects of temperature (150–190 ^oC), glycolysis time (1–4 h), ethylene glycol dosage (5–25 g), $[C_4mim][OAc]$ dosage (0.125-3.0 g) with 2.0 g PET on the glycolysis reaction were examines and under optimal conditions, complete (100%) degradation of PET and formation of BHET with a yield of 58.2%, respectively, with 1.0 g $[C_4mim][OAc]$, 20 g EG, and 3.0 g PET at 190 ^oC for only 3 h. Moreover, the mechanism for glycolysis was proposed and is shown in **Fig. 1.12** with high catalytic activity of $[C_4mim][OAc]$ was attributed to the $[CH_3COO]^-$ anion interacting with the hydrogen of the hydroxyl-group of EG and the $[C_4mim]^+$ cation interacting with the oxygen in the ester of PET.

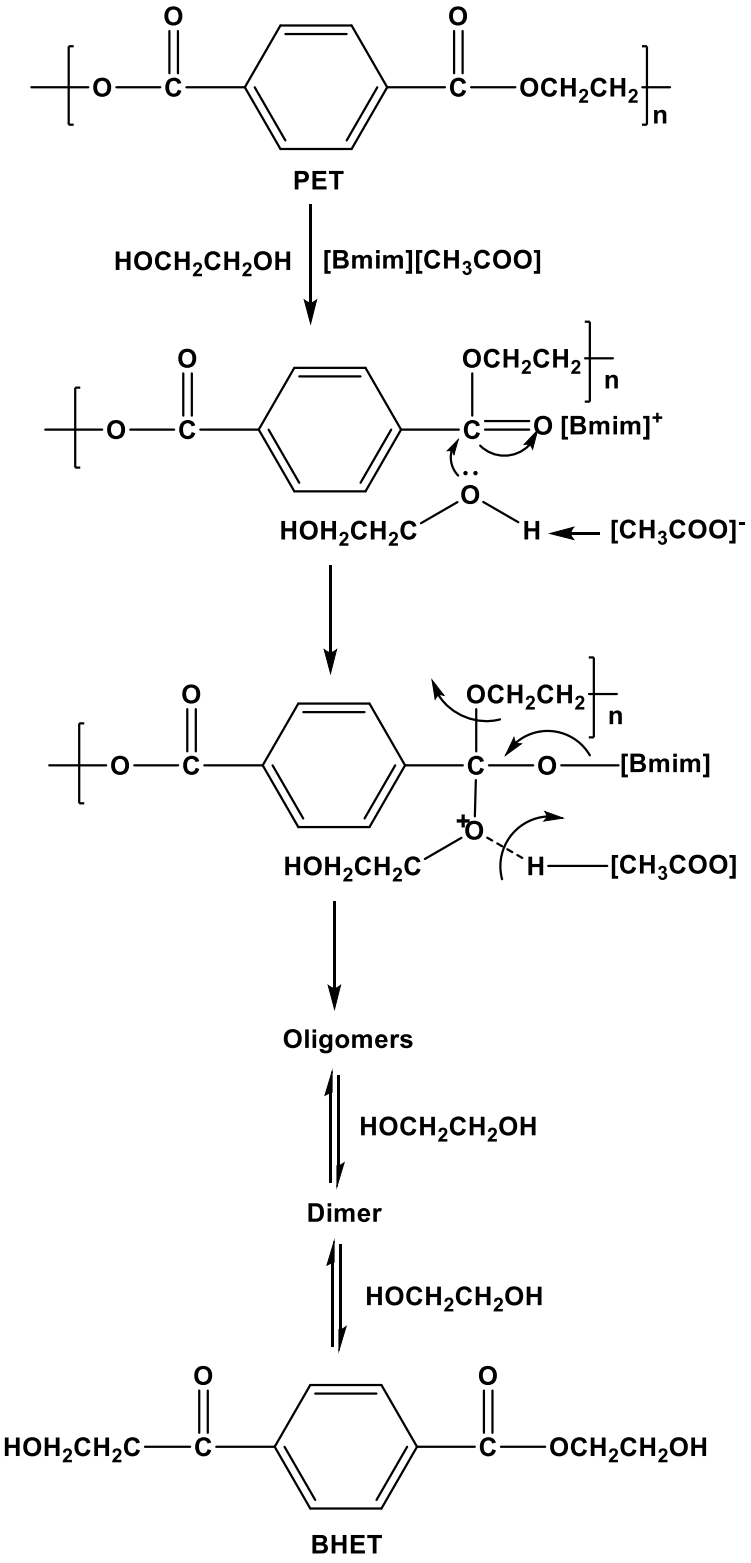


Fig. 1.12 Mechanism of the glycolysis of PET catalyzed by [C_4mim][OAc].[54]

In addition to the development of ionic liquids and metal salts as catalysts in the glycolysis reaction or other transesterification reactions, in 2002, Connor

et al.[57] first presented N-heterocyclic carbenes as catalysts for ring-opening polymerization of cyclic esters avoiding the use of transition metal initiating compounds in the polymerization. Ionic liquids as “greener” alternatives to chemical processes have obtained increasing interest. And among different types of ionic liquids, 1,3-dialkylimidazolium ionic liquids function not only as solvents but can be deprotonated to generate actively nucleophilic N-heterocyclic carbenes (NHCs) have attracted great attention.[36] Kamber et al.[36] in 2010 reported that N-heterocyclic carbenes, prepared by deprotonation of imidazolium ionic liquids could catalyze the glycolysis of PET in 1 h at atmospheric pressure in refluxing anhydrous tetrahydrofuran to afford BHET (**Fig. 1.13**).

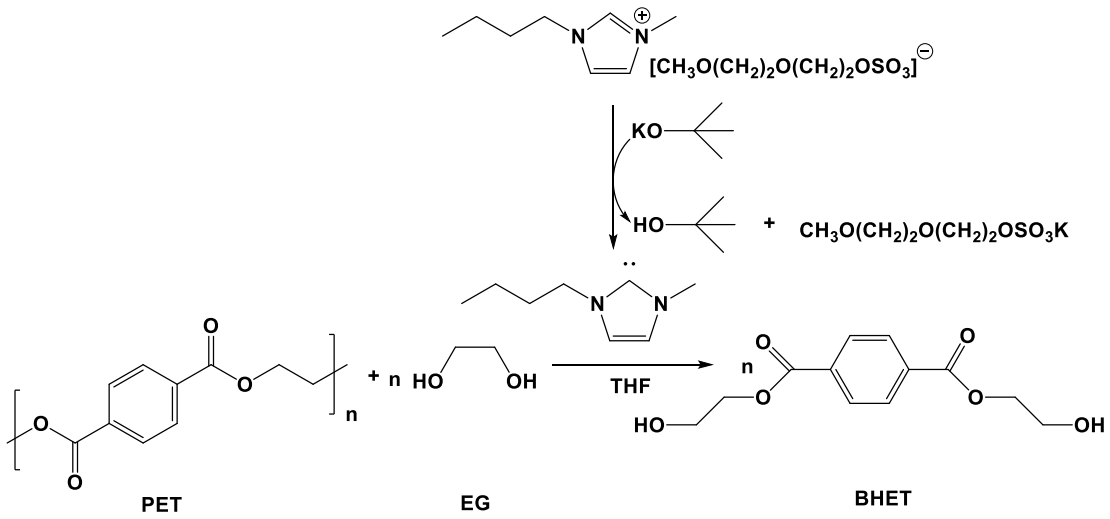


Fig. 1.13 Reaction of the degradation of PET using N-heterocyclic carbene.[36]

1.5 N-Heterocyclic Carbenes

1.5.1 Synthesis of N-Heterocyclic carbene

For a long time, N-Heterocyclic carbenes (NHCs) with lone pairs of electrons and special structure are of great interest. In 1991, Arduengo et al.[58] first synthesized and isolated colourless crystalline 1,3-di-1-adamantylimidazol-2-ylidene from the deprotonation of the corresponding imidazolium salt (1,3-di-

1-adamantylimidazolium chloride) in THF with sodium hydride in the presence of catalytic dimsyl anion ($^{-}CH_2S(O)CH_3$) at room temperature. In the latter report, Arduengo and his co-workers[59] synthesized four new stable nucleophilic N-Heterocyclic carbenes. Since then, the method using imidazolium salts as starting sources for NHC formation, strong bases such as sodium hydride or potassium tert-butoxide (^{t}BuOK) as the deprotonation reagent in THF or DMSO solvents has been widely used in many reports.

1.5.2 Application of N-Heterocyclic carbenes

In the past few decades, NHCs have been widely used not only as powerful ligands of transition metals[60] but also as organocatalysts in various molecular reactions including transesterifications, the benzoin condensation,[61] synthesis of polyurethanes,[62] and preparation of polycarbonates[63]. Especially, in the transesterification, NHCs act as efficient catalysts mediating the ring-opening polymerization of cyclic esters, the depolymerization of polyesters, and the step-growth polymerization of esters have attracted a great deal attention. In 2002, Grasa and his co-workers[64] first disclosed a versatile catalytic method to synthesize various esters using imidazol-2-ylidenes NHCs as nucleophilic catalysts in a transesterification. Nyce et al.[65] demonstrated that NHCs are efficient catalysts in transesterification reactions with primary alcohols (**Fig. 1.14**) and found that these catalysts were mild, selective, and more active than traditional organic nucleophiles; They also described the utility of NHC catalysts for polymerization reactions from DMT to PET. Kiesewetter et al.[66] in 2010 proposed the utilization of NHCs as organocatalysts in ring-opening polymerization, zwitterionic polymerization, and polybenzoin condensation.

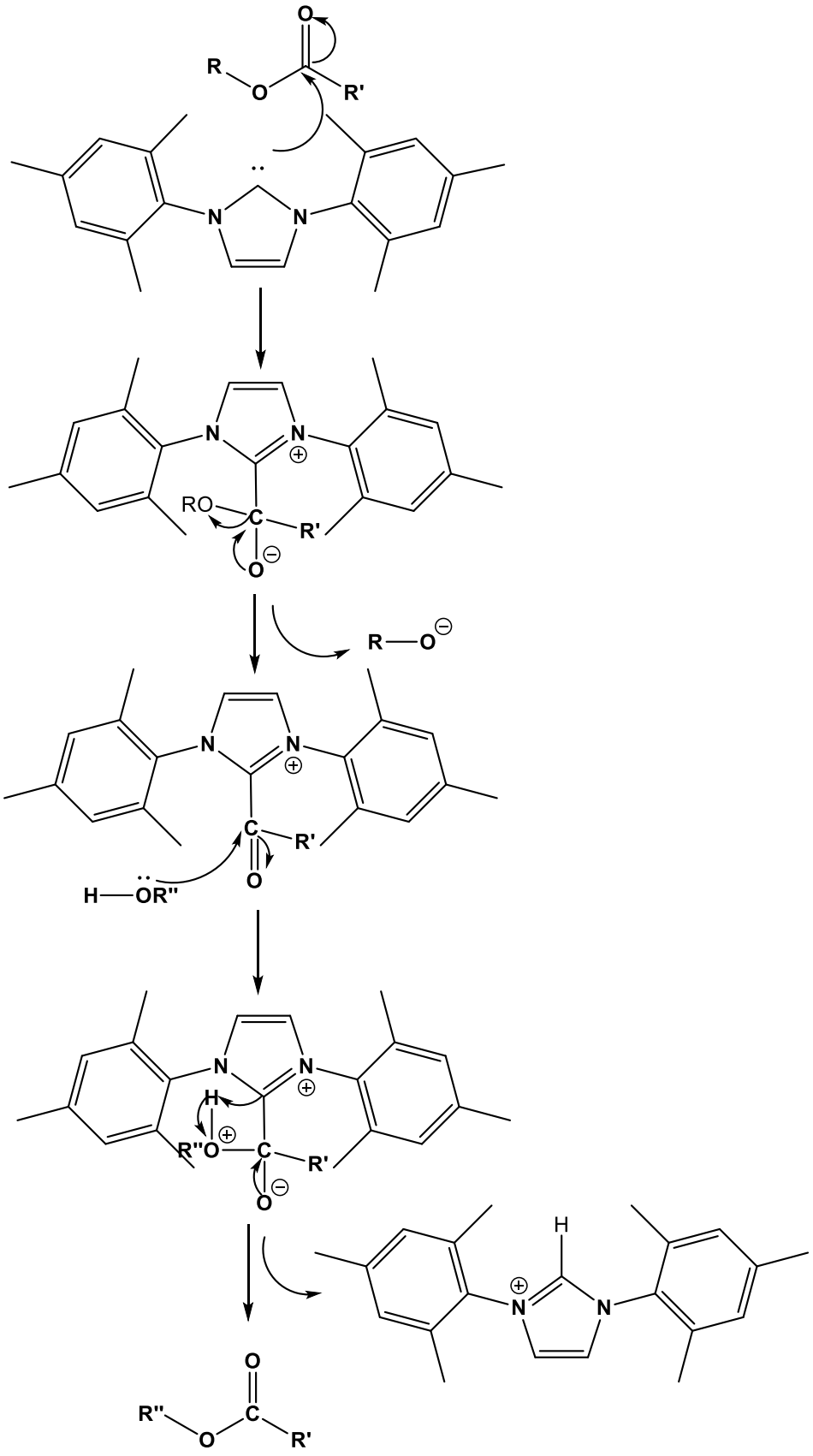


Fig. 1.14 Mechanism of N-heterocyclic carbene in transesterification.[65]

Considering previous reports about NHCs as catalysts in transesterification, we attempted to use NHCs as catalysts for the PET glycolysis reaction which is one of the transesterification reactions. **Fig. 1.15** illustrates the mechanism of N-heterocyclic carbene for the glycolysis of PET. The carbene with two unshared valence electrons nucleophilic attacks on carbon atom in the ester of PET. Finally, in the presence of ethylene glycol (EG), the imidazolium ionic liquid with active C2-hydrogen is formed; it can be converted into carbene at high temperature to achieve the recycle of N-heterocyclic carbene in the glycolysis of PET.

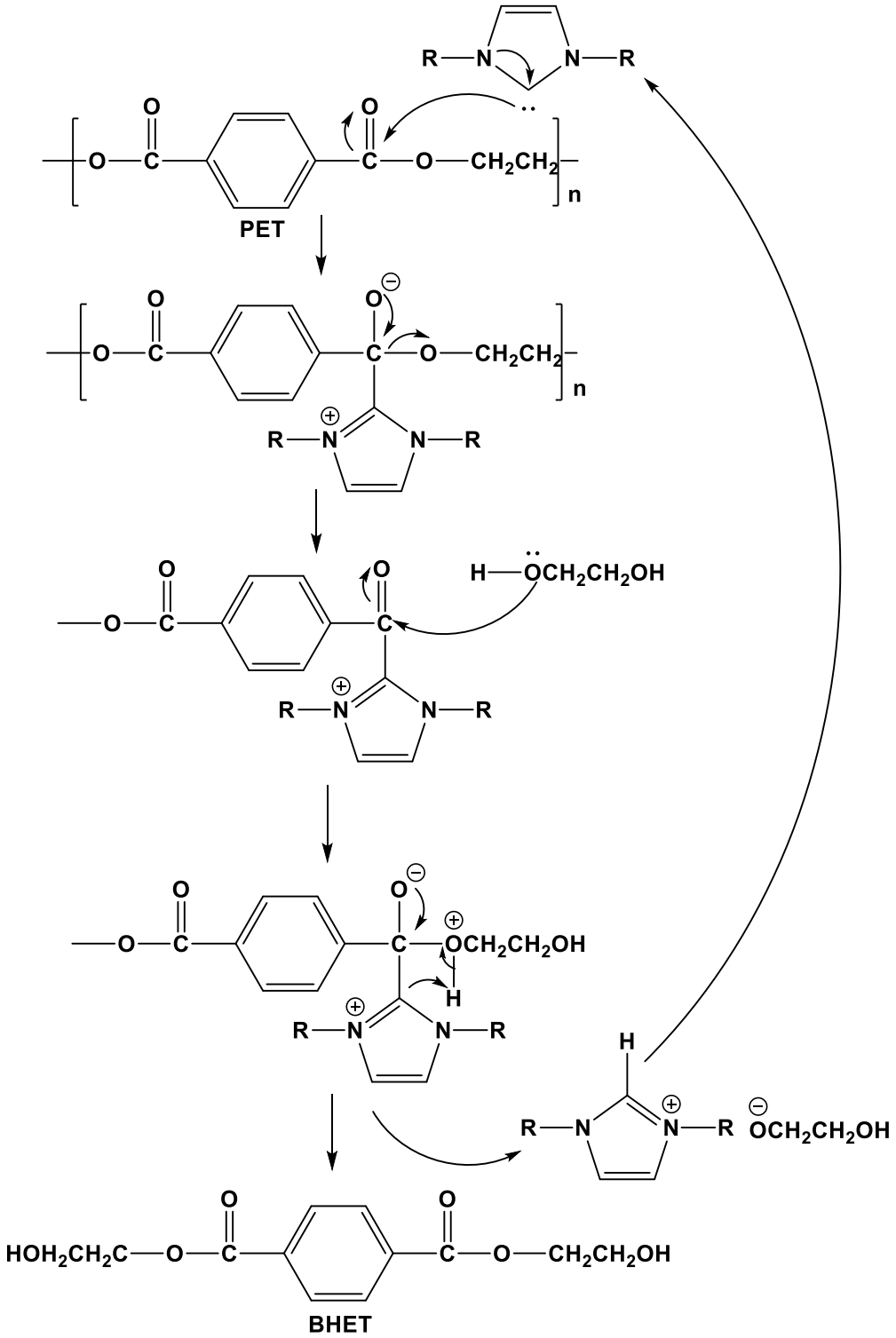


Fig. 1.15 Mechanism of N-heterocyclic carbene for the glycolysis of PET.

However, free NHCs are all extremely air- and moisture-sensitive. As a matter of fact, NHCs must generally be stored and manipulated under inert and dry conditions which limit the development of the NHCs. So, various NHC adducts which invert NHCs into NHCs masked forms to protect NHC have been studied, such as, NHC-Ag(I) complexes, NHC-CO_2 adducts, thiocarboxylates (COS), thioisocyanates (NCS), carboxylic acid, alkoxy, trichloromethyl, and imidazolium hydrogen carbonates as NHC precursors.[67]

1.5.3 A novel zwitterionic catalyst

Among these NHC precursors, stable NHC-CO_2 adducts (with the archetype being the 1,3-dimethylimidazolium-2-carboxylate zwitterion) have been developed to thermally liberate NHCs[68] which can be effective 'super-basic' catalysts for ambient temperature transesterification chemistry.[65] NHC-CO_2 adducts, 1,3-disubstituted imidazolium-2-carboxylates, can be readily prepared synthetically, are isolable, air- and water-stable reagents that can function as "protected" carbene precursors;[69] They can be considered as zwitterionic compounds formed by the nucleophilic attack of NHCs on the weak electrophilic carbon center of a CO_2 molecule. Zwitterionic imidazolium-2-carboxylates, derived from ionic liquids were first reported by Holbrey et al.[70] who described the synthesis of 1,3-dimethylimidazolium-2-carboxylate by combined N-alkylation and C-carboxylation of 1-methylimidazole with dimethyl carbonate (DMC) (**Fig. 1.16**) rather than by formation of the corresponding (unstable) NHC and then reaction with CO_2. Subsequently, Rijksen et al.[71] synthesized 1-ethyl-3-methylimidazolium-2-carboxylate (C_2mim-2-CO_2). In 2011, Li et al.[72] presented the synthesis of 1,3-dialkylimidazolium-2-carboxylates with 1-alkylimidazole and dimethyl carbonate (DMC) at 80-90 ^{o}C.

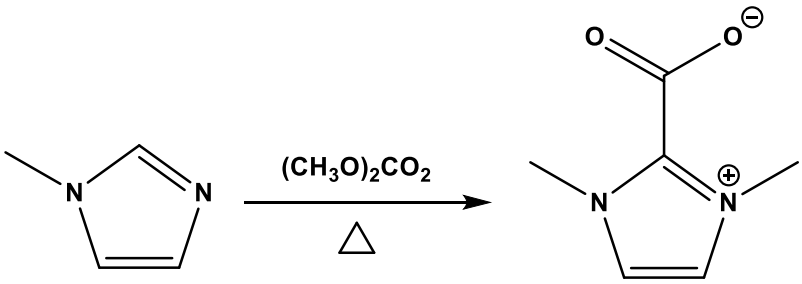


Fig. 1.16 Synthesis of 1,3-dimethylimidazolium-2-carboxylate.

In recent reports, imidazolium-2-carboxylates as pre-catalysts were used in transesterification reactions. For instance, Naik et al.[73] in 2009 used 1-n-butyl-3-methylimidazolium-2-carboxylate (C_4mim-2-CO_2) as the catalyst to convert glycerol via catalytic transesterification, achieving a 100% glycerol carbonate (GC) yield within 80 min. Naik and co-workers[63] in 2012 synthesized the 1-n-butyl-3-methylimidazolium-2-carboxylate (C_4mim-2-CO_2) with 1-n-butylimidazole and dimethyl carbonate (DMC) in methanol under argon atmosphere and used this as a catalyst precursor for the synthesis of aliphatic polycarbonates by cyclisation of diols with dimethylcarbonate through two transesterification steps of the diol with methylcarbonate. Likewise, in 2013, Hoppe et al.[74] used 1-n-butyl-3-methylimidazolium-2-carboxylate as a precatalyst for the ring-opening polymerization of ε-caprolactone and *rac*-lactide under solvent-free conditions, replicating the NHC catalyzed polymerization previously reported.[36] Stewart et al[75] in 2015 synthesized bio-based cyclic carbonate using 1,3-dialkylimidazole-2-carboxylate as pre-catalyst.

NHC-CO_2 adducts (imidazolium-2-carboxylates) are stable at room temperature, however, at high temperature, they can decompose to release CO_2 and form free NHCs. Van Ausdall et al.[69] reported that simple N-alkyl and N-aryl imidazole carbenes could be generated from deprotonation of imidazolium salt with potassium hexamethyldisilylazide (KHMDS) in toluene

and, conversely, that imidazolium carboxylates were generated in excellent yields from direct carboxylation of the NHCs. They studied the thermal stability of NHC-CO_2 using TGA, demonstrating that the decarboxylating ability of NHC-CO_2 is largely dependent on the steric bulk on the N-substituents and that the ability of the NHC-CO_2 to decarboxylate increases as steric bulk on the N-substituent increases (**Fig. 1.17**). Likewise, Duong et al.[76] pointed out that the stability of NHC-CO_2 adducts can affect the onset temperature of a thermally induced decarboxylation. Zhou et al.[68] in 2008 investigated the thermal stability of NHC-CO_2 adducts in solution in organic solvents and found that saturated imidazolinium carboxylates exhibited higher thermal stability in the presence of free CO_2 which can effectively inhibit thermal decomposition of NHC-CO_2 adducts. Wang et al.[77] researched decarboxylation of NHC-CO_2 and proposed that two processes (decarboxylation and decomposition) occur when N-substituents are aryl group in the range of temperature 50-350 ^oC while the initial temperatures of mass loss are lower when the N-substituents are alkyl group and no decomposition occurs.

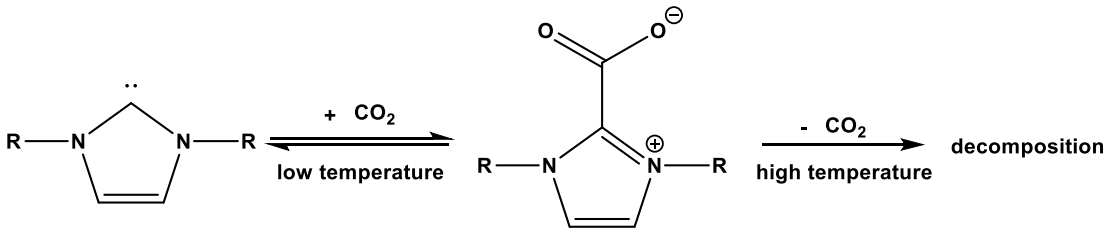


Fig. 1.17 The synthesis and decomposition of 1,3-disubstituted-2-imidazolium carboxylates.[69]

1.6 Objective

Considering the carbene as an efficient catalyst in the transesterification reaction and the carboxylate as a stable pre-catalyst or precursor which can decarboxylate to release CO_2 and form carbene at high temperature, novel zwitterions as catalysts for PET glycolysis were studied. In this project, the ionic liquid 1,3-dibutylimidazolium acetate and 1,3-dibenzylimidazolium chloride were synthesized firstly. Then the synthesized ionic liquids were transferred into relative carbene with strong base sodium hydride and solvent non-aqueous THF. Finally, the carbenes were converted into carboxylate when reacting dry CO_2. Another route was that using 1-methylimidazole and dimethyl carbonate directly generated 1,3-dimethylimidazolium-2-carboxylate. After that, the synthesized carboxylate was used as catalyst for the glycolysis of PET to test the possibility of reaction and study the effect of reaction reactions (reaction temperature, reaction time, weight ratio of PET:EG, weight ratio of PET:catalyst) on the conversion of PET, yield of BHET and the selectivity of BHET compared with the relative ionic liquid as catalyst for the glycolysis of PET.

Chapter 2

Experimental

2.1 The synthesis of ionic liquid

2.1.1 1,3-dibutylimidazolium acetate

Butylamine (3.66 g, 0.05 mol, 2 eq.) was added into a 250 ml, three-necked, round-bottomed flask equipped with two dropping funnels, a reflux condenser, and a magnetic stirrer bar. The reaction was controlled by immersing the flask in an ice bath while adding formaldehyde (37 wt% in water, 2.03 g, 1 eq.) and acetate acid (2.25 g, 1.5 eq.) dropwise simultaneously. The mixture was stirred for 30 min at 0 ^{o}C, after which the glyoxal (40 wt% in water, 3.63 g, 1 eq.) was added and reaction mixture was stirred overnight at room temperature. The solution obtained after reaction was washed with diethyl ether until the organic phase became colorless and the water was removed by rotary evaporator at 60 ^{o}C. The concentrated product was dried in a Schlenk at 60 ^{o}C overnight.[78] The products were analyzed using nuclear magnetic resonance (NMR) spectroscopy.

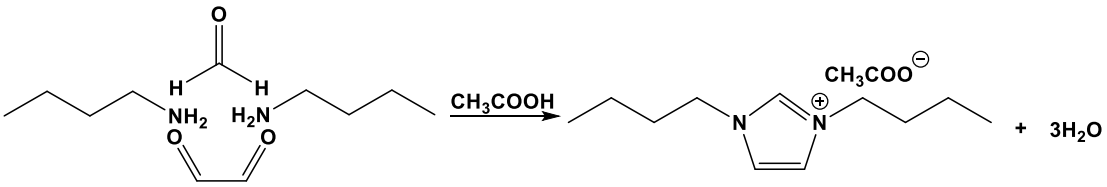


Fig. 2.1 The “one-pot cyclisation” pathway of 1,3-dibutylimidazolium acetate.

1,3-dibutylimidazolium acetate was isolates as a dark orange oil (5.34 g, 0.022 mol, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm)：11.49 (s, 1H, CH), 7.11(s, 2H, 2CH), 4.35 (t, J = 7.4 Hz, 4H, $2CH_2$-N), 2.02 (s, 3H, CH_3), 1.85 (m, 4H, $2CH_2$-CH_2), 1.37 (m, 4H, $2CH_2$-CH_2), 0.94 (t, 6H, $2CH_3$-CH_2). ^{13}C NMR (100

MHz, $CDCl_3$, δ/ppm): 177.40 (C=O), 140.44 (N-CH-N), 121.07 (2CH-N), 49.68 ($2CH_2$-N), 32.14 ($2CH_3$), 24.48 ($2CH_2$), 19.71 ($2CH_2$), 13.64 (CH_3).

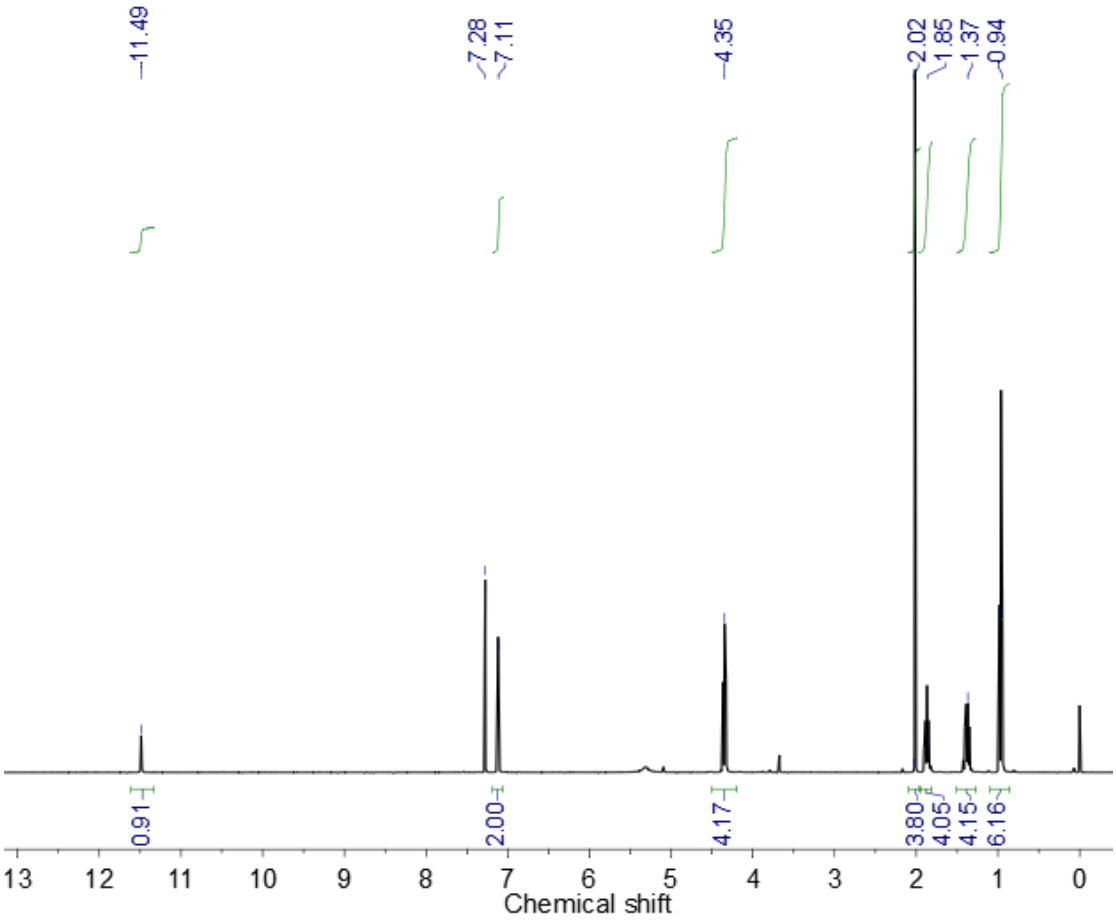


Fig. 2.2 ^{1}H-NMR spectrum in D_2O of 1,3-dibutylimidazolium acetate.

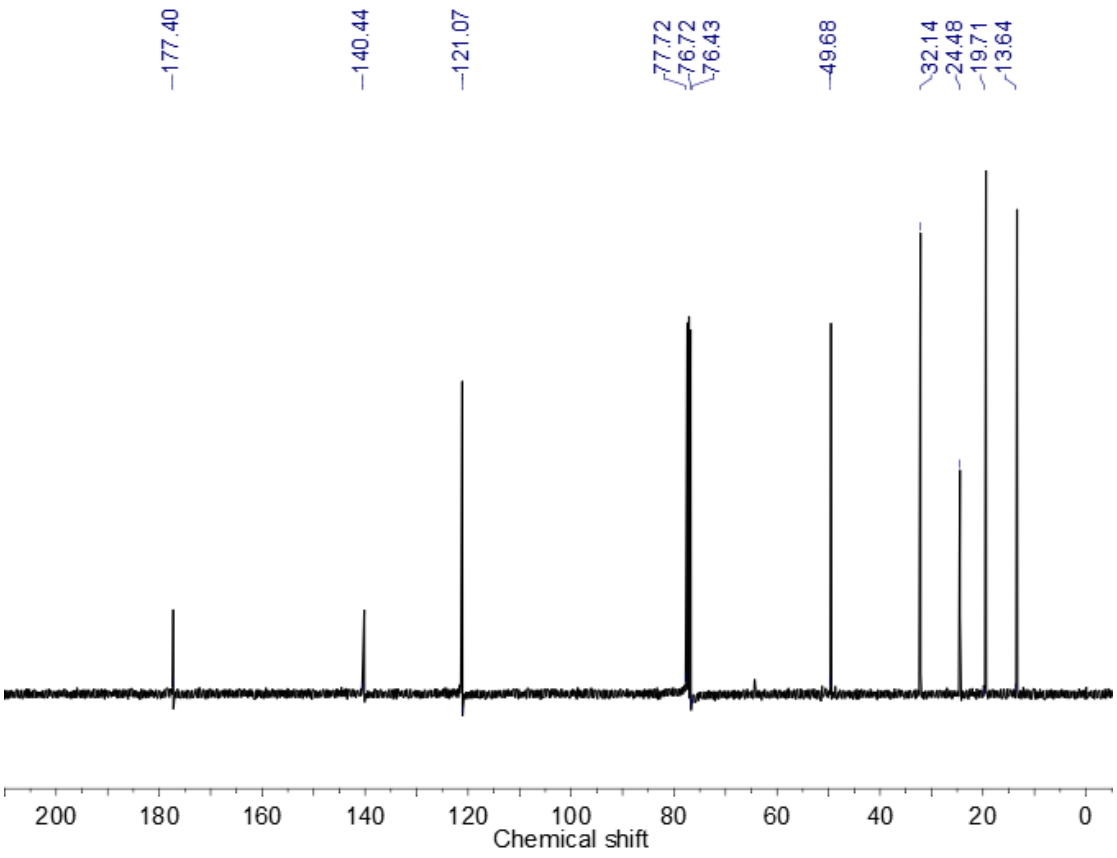


Fig. 2.3 ^{13}C NMR spectrum in D_2O of 1,3-dibutylimidazolium acetate.

2.1.2 1,3-dimethylimidazolium acetate

Methylamine (1.55 g, 0.05 mol, 2 eq.) was added into a 250 ml, three-necked, round-bottomed flask equipped with two dropping funnels, a reflux condenser, and a magnetic stirrer bar. The reaction was controlled by immersing the flask in an ice bath while adding formaldehyde (37 wt% in water, 0.751 g, 1 eq.) and acetate acid (2.25 g, 1.5 eq.) dropwise simultaneously. The mixture was stirred for 30 min at 0 °C, after which the glyoxal (40 wt% in water, 1.45 g, 1 eq.) was added and reaction mixture was stirred for 6 h at room temperature. The solution obtained after reaction was washed with diethyl ether until the organic phase became colorless and the water was removed by rotary evaporator at 60 °C. The concentrated product was dried in a Schlenk at 60 °C overnight. The products were analyzed using nuclear magnetic resonance (NMR)

spectroscopy.

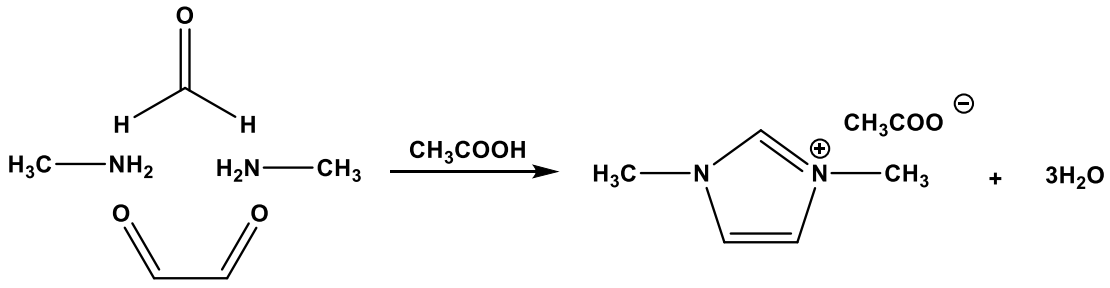


Fig. 2.4 The “one-pot” cyclisation pathway of 1,3-dimethylimidazolium acetate.

1,3-dimethylimidazolium acetate was isolated as a dark orange oil (3.43 g, 0.022 mol, 88%). ^{1}H-NMR (400 MHz, D_2O, δ/ppm): 8.52 (s, 1H, CH), 7.29 (s, 2H, 2CH), 3.75 (s, 6H, $2CH_3$), 1.74 (s, 3H, CH_3). ^{13}C NMR (100 MHz, D_2O, δ/ppm): 180.62(C=O), 136.50 (N-CH-N), 123.36 (2CH-N), 35.02 ($2CH_3$), 23.22 (CH_3).

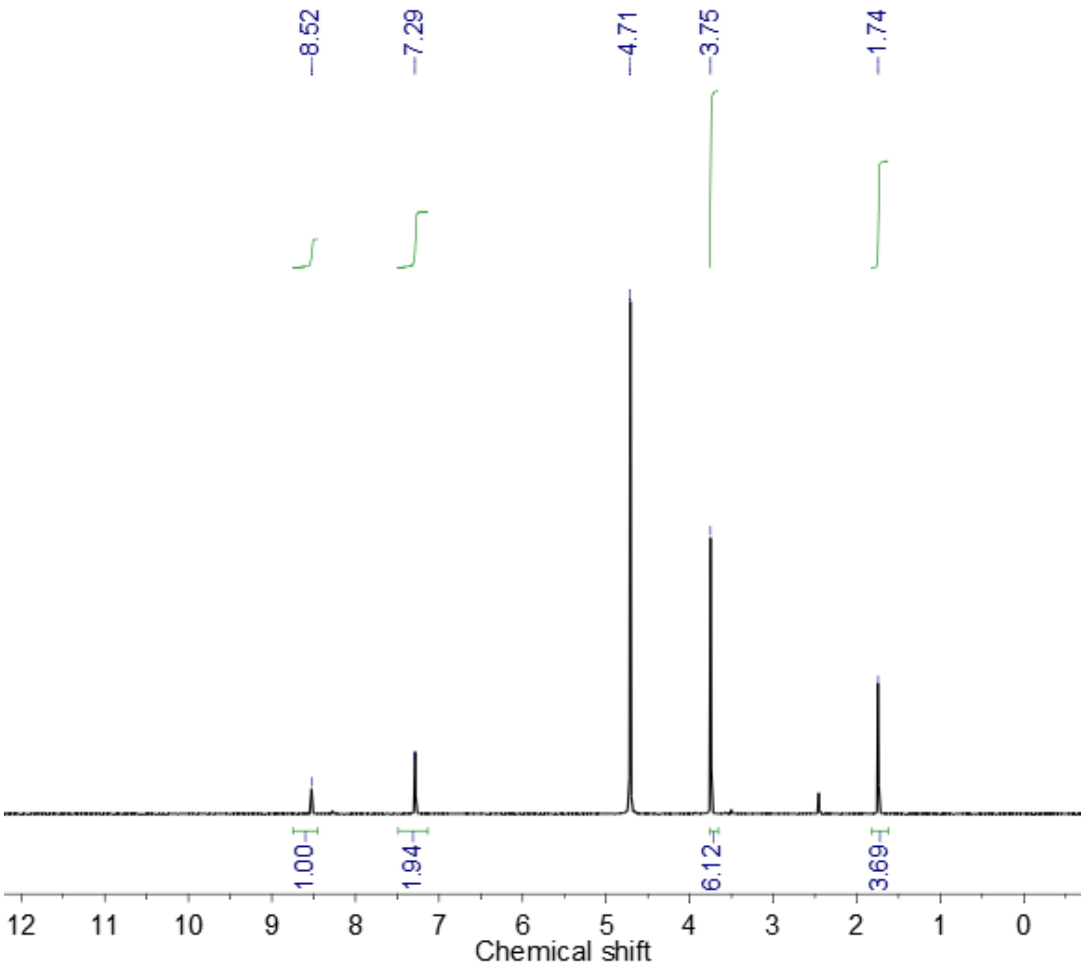


Fig. 2.5 ^{1}H-NMR spectrum in D_2O of 1,3-dimethylimidazolium acetate.

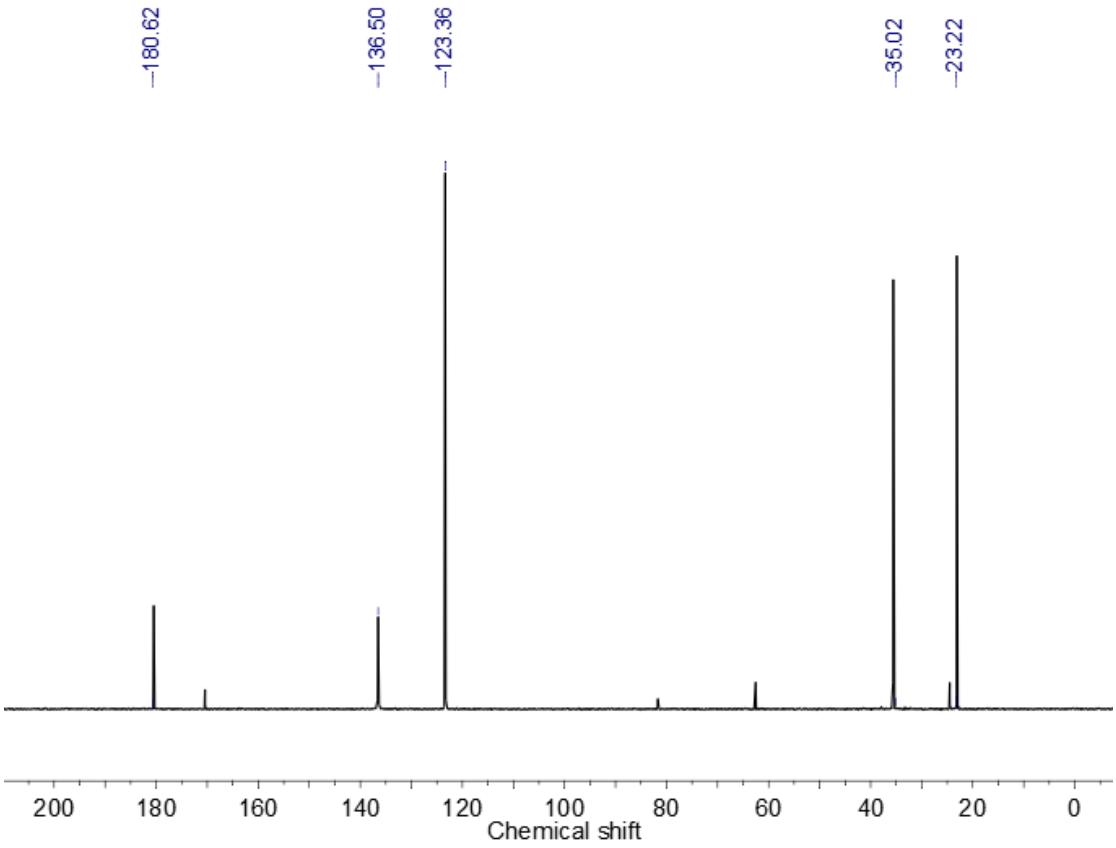


Fig. 2.6 ^{13}C NMR spectrum in D_2O of 1,3-dimethylimidazolium acetate.

2.1.3 1,3-dibenzylimidazolium chloride

A three-neck round bottom flask equipped with a magnetic stirrer and a condenser was placed in an ice bath. It was charged with imidazole (0.68 g, 0.01 mol, 1 eq.) and 10 ml THF and then left under stirring for five minutes. After the temperature leveled off, sodium hydride (60% in oil, 0.8 g, 2 eq.) was added to the flask. After 2 h, the ice bath was removed and then benzyl chloride (1.27 g, 1 eq.) was delivered dropwise to the round-bottom flask. After the completion of the addition, the reaction was left for 18 h under constant stirring in oil bath at 50 ^oC until a light-yellow slurry was formed. The mixture was cooled at room temperature and then diethyl ether was added to remove salts through filtration. The liquid obtained was transferred to a one-neck round-bottom flask and evaporated in vacuo. The 1-benzylimidazole

formed in this way was washed three times with 20 ml diethyl ether to remove the excess benzyl chloride and evaporated in vacuo to obtain light yellow solid which was afterwards dried in vacuo overnight.

1-benzylimidazole (3.16 g, 1 eq.) and 20 ml THF were added into in a three-neck round bottom flask with a magnetic stirrer and a condenser. A slight excess of benzyl chloride (3.8 g, 1.5 eq.) was delivered dropwise into the flask and then the mixture was heated at 50 °C in oil bath. After 20 h, the reaction was stopped and cooled at room temperature. Diethyl ether was added into the mixture and then it was filtered to remove the salts. The liquid was evaporated in vacuo and dried in a Schlenk at 60 °C overnight. The products were analyzed using nuclear magnetic resonance (NMR) spectroscopy.

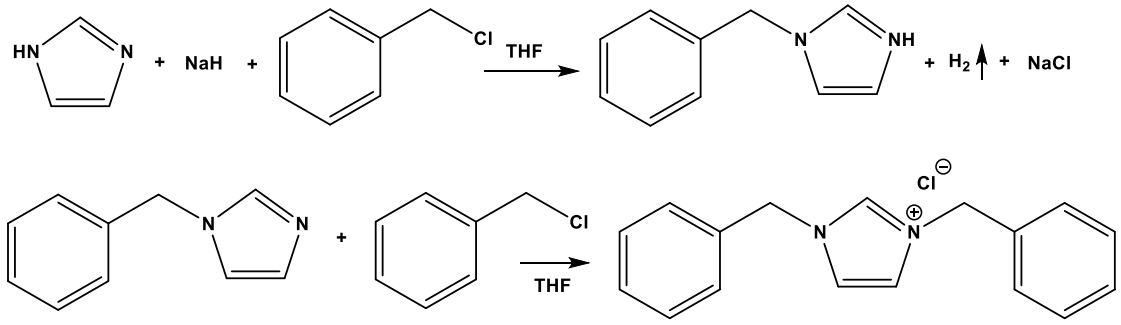


Fig. 2.7 The alkylation pathway of 1,3-dibenzylimidazolium chloride.

1,3-dibenzylimidazolium chloride was obtained as a light yellow oil (3.6 g, 0.013 mol, 63.4%). ^{1}H NMR (400 MHz, DMSO, δ/ppm): 9.66 (s, 1H, N-CH-N), 7.89 (d, *J* = 1.6 Hz, 2H, 2CH), 7.47 – 7.39 (m, 10H), 5.48 (s, 4H, 2N-CH_2-C). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 136.39 (N-CH-N), 133.38, 129.24, 128.62, 128.25, 122.11, 52.39 (N-CH_2-Ph).

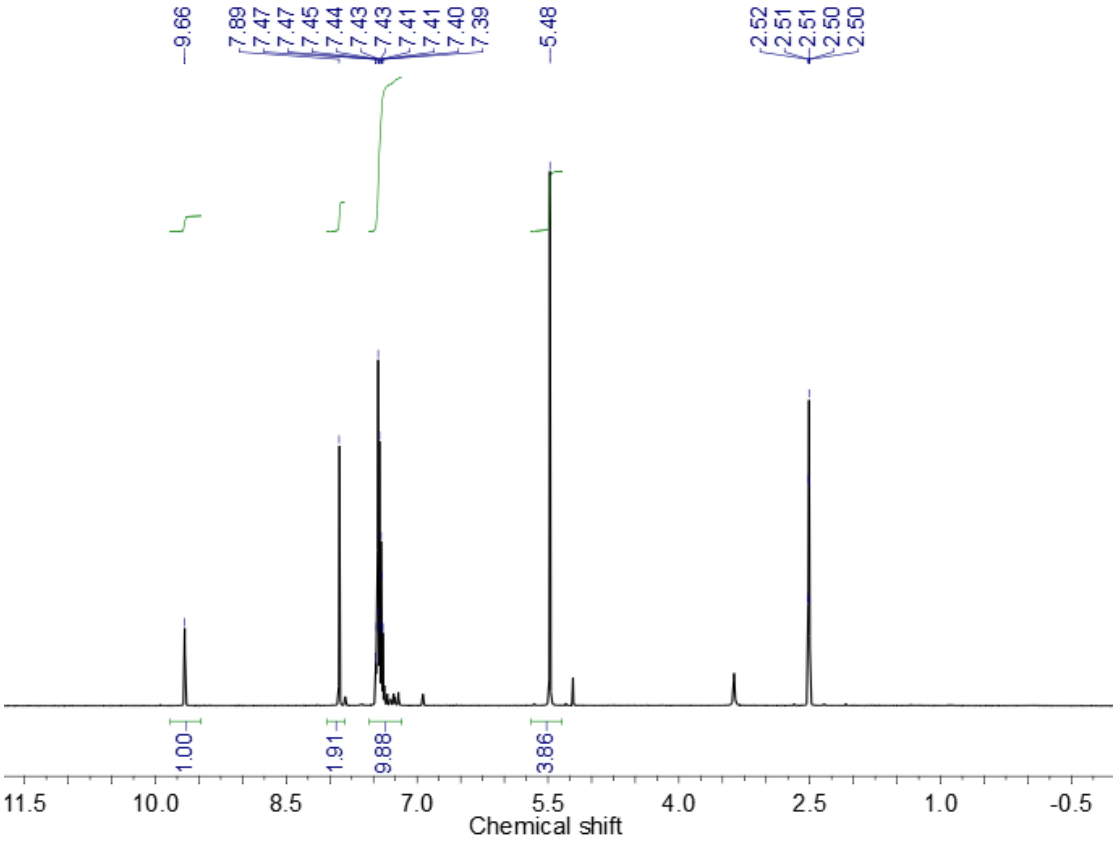


Fig. 2.8 ^{1}H-NMR spectrum in DMSO-d_6 of 1,3-dibenzylimidazolium chloride.

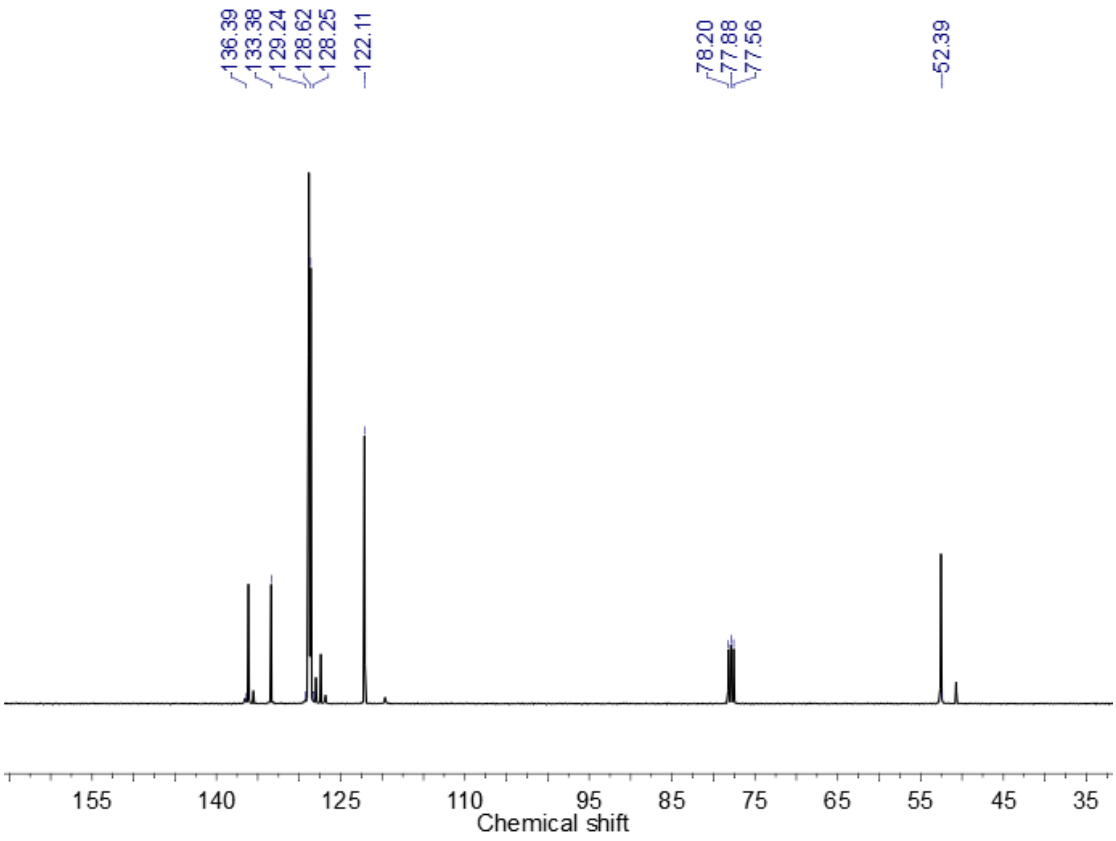


Fig. 2.9 ^{13}C NMR spectrum in $CDCl_3$ of 1,3-dibenzylimidazolium chloride.

2.2 Synthesis of 1,3-dialkylimidazolium-2-carboxyalte zwitterions

2.2.1 1,3-dimethylimidazolium-2-carboxylate

1-methylimidazole (10 ml, 0.12 mol) and dimethyl carbonate (15 ml, 0.18 mol) were added into a sealed 30 ml screw top pressure tube. The mixture was stirred in an oil bath for 72 h at 90 ^oC. After the allowed time, the reaction was placed to cool down to room temperature and the screw cap was carefully removed. The clear supernatant liquid was poured off and the remaining white precipitate were stirred in 30 ml diethyl ether for 30 min. The white precipitate was then filtered and washed with diethyl ether (2 x 15 ml), acetone (2 x 15

ml), and acetonitrile (2 x 15 ml). The remaining white solids were dried under vacuum. The products were analyzed using nuclear magnetic resonance (NMR) spectroscopy, and thermogravimetric analysis (TGA) (temperature range: 20-260 ^{o}C, heating rate: 10 ^{o}C, gas: N_2).

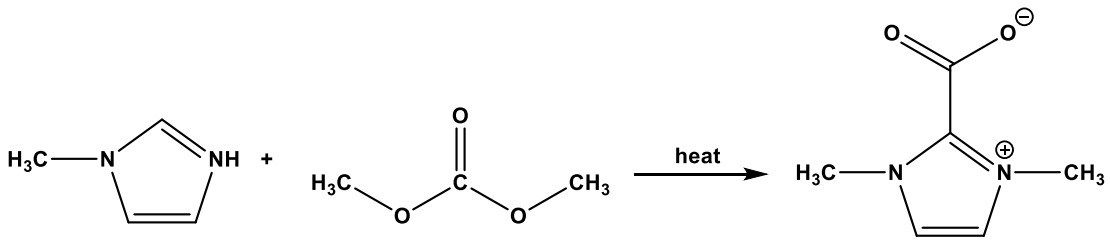


Fig. 2.10 The synthesis of 1,3-dimethylimidazolium-2-carboxylate.

The zwitterionic salt, 1,3-dimethylimidazolium-2-carboxylate was formed as a white crystalline solid (4.21 g, 23.87%). ^{1}H NMR (400 MHz, D_2O, δ/ppm): 7.28 (s, 2H, 2CH), 3.90 (s, 6H, 2CH_3-N). ^{13}C NMR (100 MHz, D_2O, δ/ppm): 158.60 (C=O), 139.75 (N-CH-N), 122.91 (CH-N), 36.87 (CH_3).

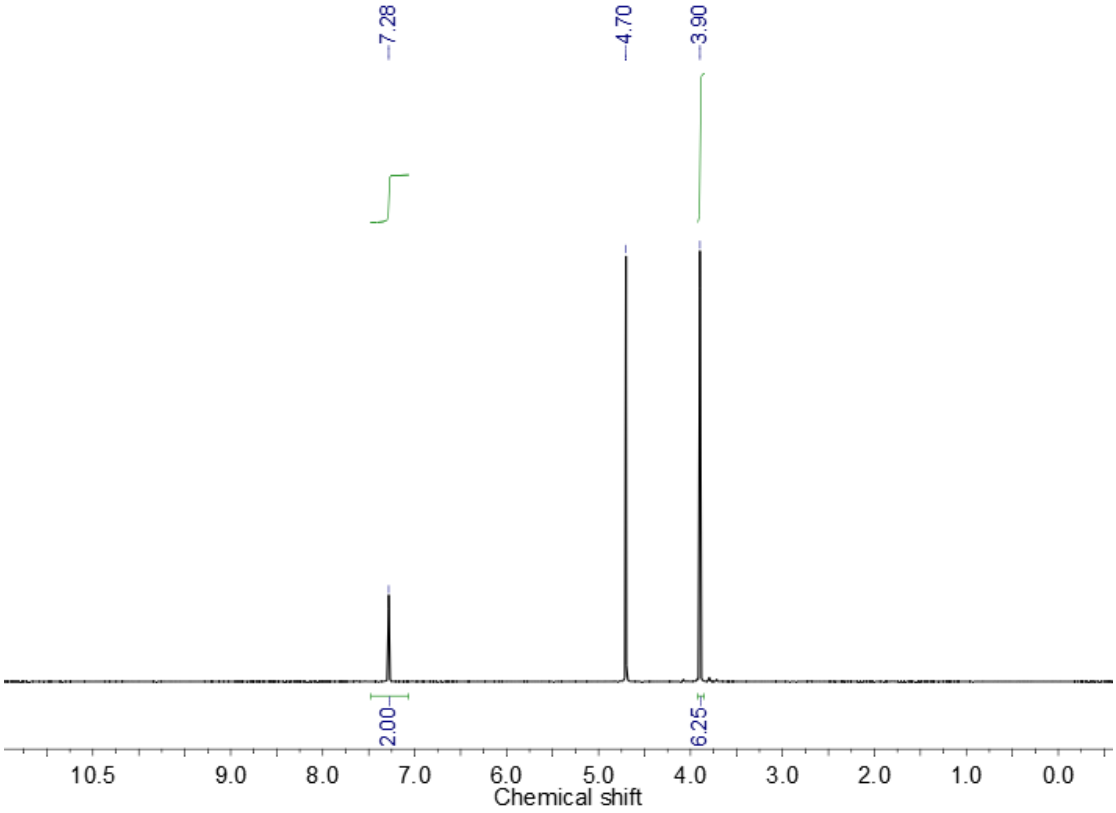


Fig. 2.11 ^{1}H-NMR spectrum in D_2O of 1,3-dimethylimidazolium-2-carboxylate.

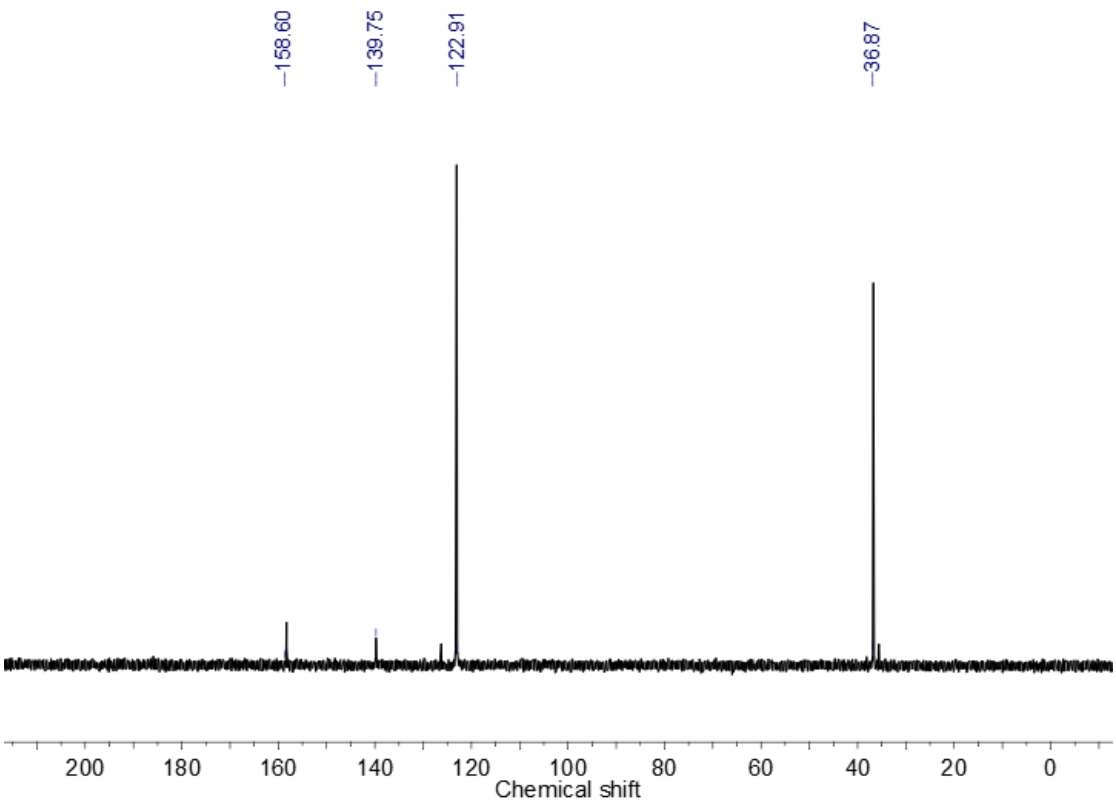


Fig. 2.12 ^{13}C NMR spectrum in D_2O of 1,3-dimethylimidazolium-2-carboxylate

2.2.2 1,3-dibutylimidazolium-2-carboxylate

Dried 1,3-butylimidazolium acetate (2.4 g, 0.01 mol, 1 eq.) and sodium hydride (60% in oil, 0.44 g, 1.1 eq.) were added into a 50 cm^3 round-bottom flask. It was heated in a Kugelrohr[79] apparatus at 120 ^oC under 500 Pa (5 mbar) reduced pressure for 1 h, and then CO2 was introduced into the Kugelrohr from a vessel filled with dry ice over 30 min. After the dry ice was charged the flask for 30 min, there was no change. It is difficult to collect the yellow oil and to do some analytical measurements.

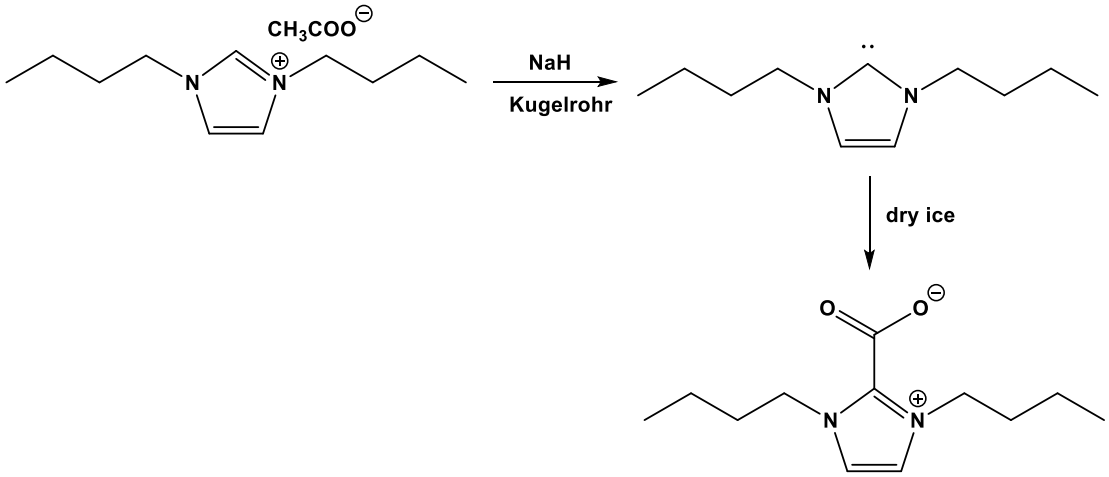


Fig. 2.13 The synthesis of 1,3-dibutylimidazolium-2-carboxylate.

2.2.3 1,3-dibenzylimidazolium-2-carboxylate

An oven-dried three-neck round-bottomed flask equipped with a magnetic stir bar fitted with three sept was charged with 1,3-dibenzylimidazolium chloride (4.3 g, 0.015 mol, 1 eq.) and sodium hydride (0.66 g, 1.1 eq, 60% dispersion in oil) under a nitrogen atmosphere.[76] Dry THF (40 ml) was then added and the reaction mixture stirred at room temperature for 4 h. Stirring was then stopped and the solution allowed to stand for 30 min until the solid suspension had settled at the bottom of the flask. The clear solution was transferred into another oven-dried flask using a syringe under nitrogen. A balloon of CO_2 was then introduced, and the solution was left for another 2 h. When the CO_2 reacted with the transferred clear solution, the color of the solution changed from red to light yellow, and there was no solid.

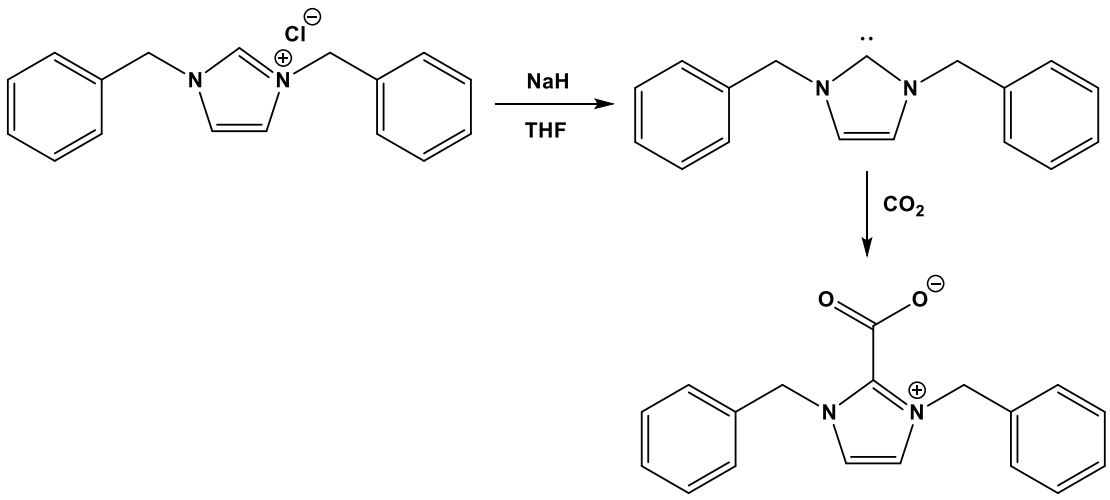


Fig. 2.14 The synthesis of 1,3-dibenzylimidazolium-2-carboxylate.

2.3 Glycolysis of PET

1.0 g of PET (cut into 4 x 4 mm pieces) from post-consumer plastic bottle, a certain amount of ethylene glycol (5-20 g), and a certain amount of catalysts (1,3-dimethylimidazolium-2-carboxylate or 1,3-dimethylimidazolium acetate ionic liquid) (0.05-0.4 g) were loaded into a 50 ml round-bottom three-necked flask equipped with a thermometer and a reflux condenser. The reaction mixture was stirred under nitrogen at reaction temperature ranging from 160 to 200 ^{o}C for 0.5-4 h. The flask was immersed in oil bath at a specific temperature for the required time. In this glycolysis reaction, the ethylene glycol and the catalyst were preheated to the selected temperature (160-200 ^{o}C) prior to the addition of the PET to minimize the time required to reach the reaction temperature. When the glycolysis reaction was complete, the un-depolymerized PET was quickly separated from the liquid phase before the products precipitated. The un-depolymerized PET was washed with 20 ml methanol which was then mixed with the liquid fraction. The remaining PET was washed, dried and weighed. The conversion of PET is defined as.[54]

$$\text{Conversion of PET} = \frac{W_0 - W_1}{W_0} \text{ X } 100\%$$

Where W_0 represents the initial weight of PET and W_1 represents the weight of un-depolymerized PET.[54] Meanwhile, the liquid fraction was concentrated on a vacuum rotary evaporator at 50 ^oC and then the product was stored in a refrigerator at 0 ^oC for 24 h. White crystalline flakes were formed in the filtrate, then filtrated and washed with 3 ml water and dried. The remaining reaction mixture after removing crystallized precipitated BHET contained catalyst, ethylene glycol and residual BHET. Each measurement of the polymerization of PET to monomer BHET as above was repeated 2-3 times and the average value of each measurement was shown in **Results and Discussion** Tables. In order to investigate that the catalyst can be recycled more than one time, 5 g filtrate and 0.5 g PET (4 x 4 mm) was added into the flask and were heated at a certain temperature to repeat above glycolysis steps.

The product was the bis(hydroxyethyl) terephthalate (BHET) monomer. The products were analyzed using nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, gas chromatography (GC), and high performance liquid chromatography (HPLC).

The selectivity of the BHET monomer is defined as[54]

$$\text{Isolated selectivity of BHET} = \frac{W_{BHET}/MW_{BHET}}{W_{PET,D}/MW_{PET}} \text{ X } 100\%$$

And yield is defined as[54]

$$\text{Isolated yield of BHET} = \frac{W_{BHET}/MW_{BHET}}{W_{PET,I}/MW_{PET}} \text{ X } 100\%$$

Where $W_{PET,D}$, $W_{PET,I}$, and W_{BHET} refer to the weight of depolymerized PET,

the initial weight of PET, and the weight of BHET, respectively. MW_{BHET} and MW_{PET} are the molecular weights of BHET (254 g mol^{-1}) and the PET repeat unit (192 g mol^{-1}), respectively.[54]

To check whether the reaction mixture after filtering BHET contains monomer, dimer or other oligomers, the high performance liquid chromatography (HPLC) of the reaction mixture was obtained.

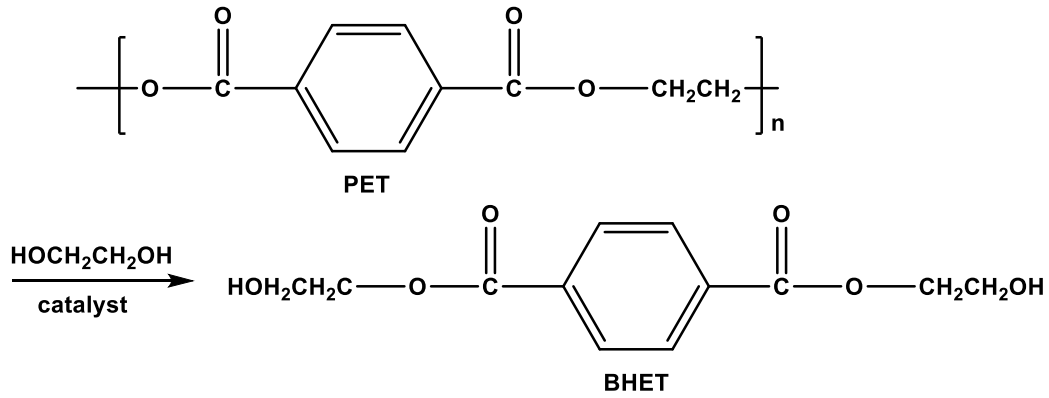


Fig. 2.15 The polymerization of PET to monomer BHET.

BHET is a white crystalline solid: ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 8.17 (s, 4H, benzene), 5.02 (s, 2H, 2OH), 4.39 (t, J = 4.37 Hz, 4H, 2CH_2), 3.78 (t, J = 3.83 Hz, 4H, 2CH_2). ^{13}C NMR (100 MHz, acetone-d_3, δ/ppm): 165.63, 134.47, 129.71, 66.79, 59.88.

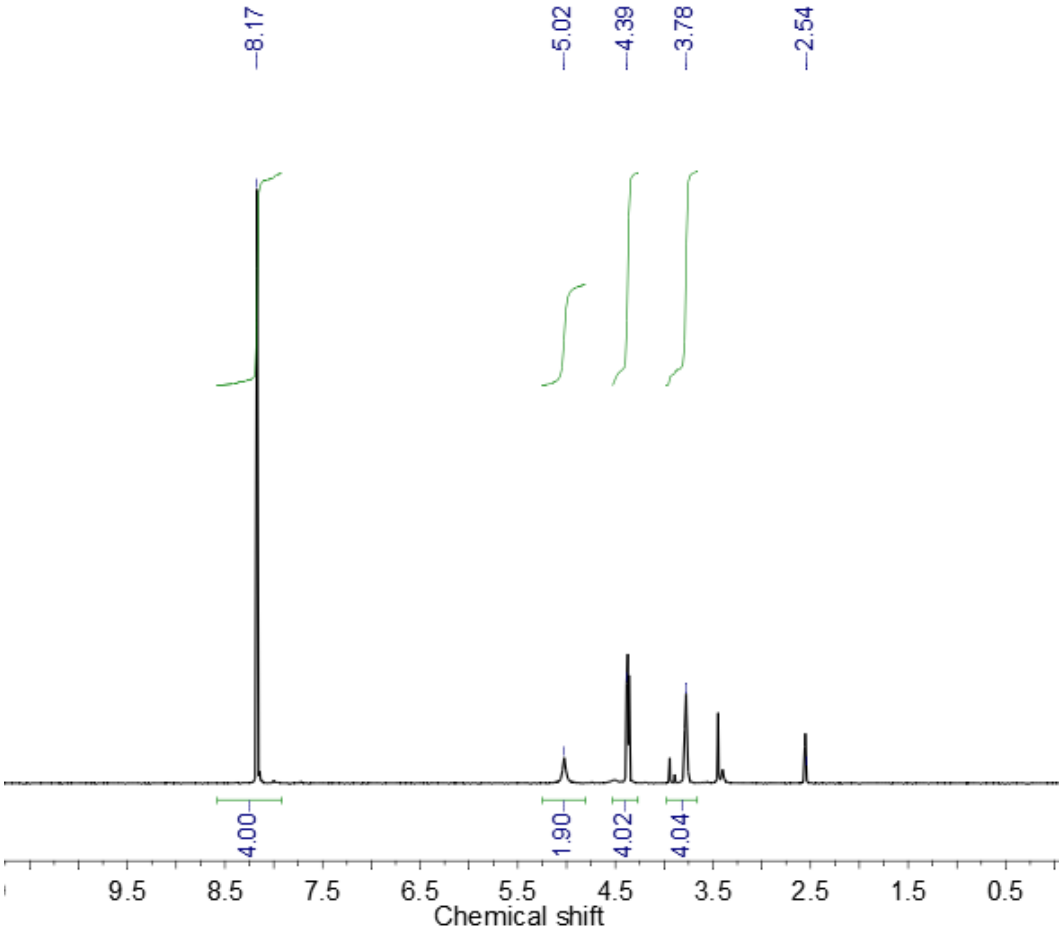


Fig. 2.16 ^{1}H NMR spectrum in DMSO-d_6 of BHET.

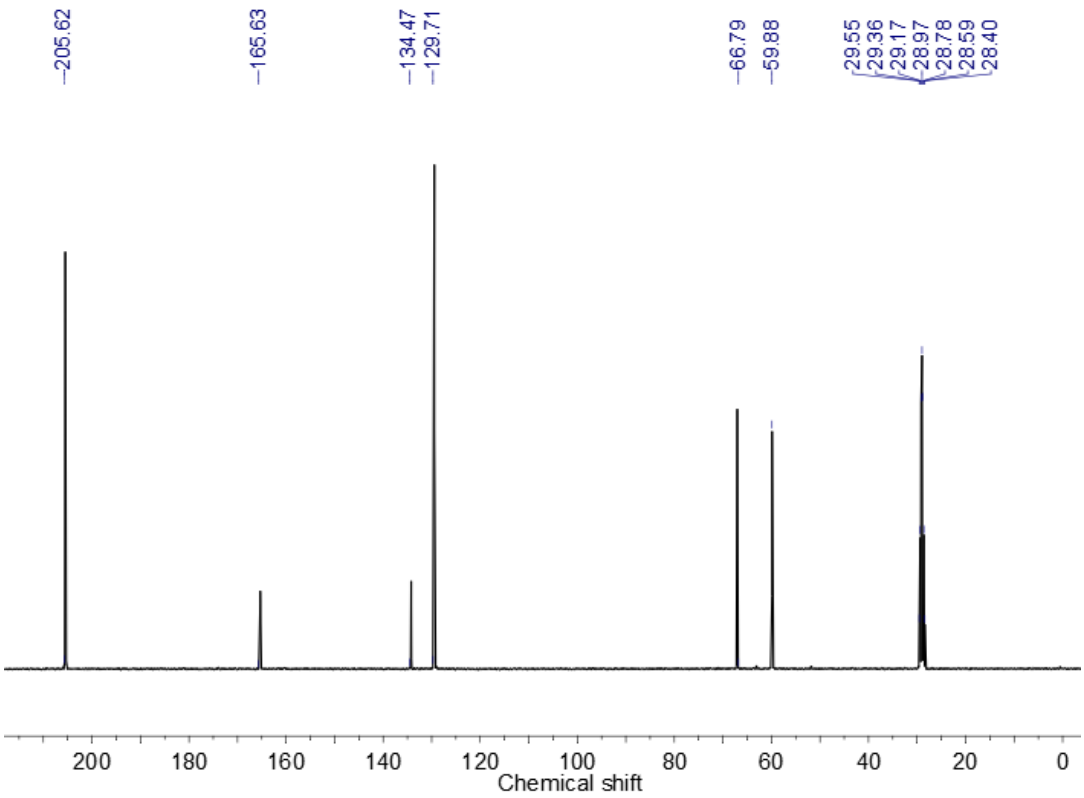


Fig. 2.17 ^{13}C NMR spectrum in DMSO-d_6 of BHET.

2.4 Characterization of products

(a) **Proton Nuclear magnetic resonance (NMR) spectra** were measured by Bruker ADVANCE 400 spectrometer at room at 400 MHz. The sample was prepared with NMR solvent (D_2O, $CDCl_3$, DMSO-d_6) in the capillaries and submitted to NMR measurement. All the post-processing and visualization are done with software MestReNove.

(b) **Fourier-transform infrared spectroscopy (FTIR) spectra- Attenuated Total Reflectance (ATR)** were measured by PerkinElmer spectrum II spectrometer with a resolution of 1 cm^{-1} and 16 accumulations. The crystal area was cleaned and the background was collected firstly. And then the solid powder material was placed onto the small crystal area. The pressure arm was positioned over the crystal/sample area and the results were start to collect in

computer.

(c) **Thermogravimetric Analysis (TGA)** was recorded by Mettler Toledo DSC/TGA Star under a nitrogen atmosphere, in the temperature range of 20-260 ^{o}C with a heating rate of 10 ^{o}C min^{-1}.

(d) **High performance liquid chromatography (HPLC)** was carried out with a Phenomenex C8 column and coupled to a UV-VIS detector operating at 254 nm. Deionized water:methanol 50%:50% was used as mixed mobile phase with a flow rate of 0.5 ml/min. The solution was prepared by dissolving about 1 mg mixture reaction in 2 ml of methanol/water (50/50 v/v) mixture.

Chapter 3

Results and Discussion

3.1 Preparation of catalysts

The main aim of this project is the synthesis of carboxylate (NHC-CO_2) as catalyst for the glycolysis of PET from the corresponding ionic liquid, sodium hydride and CO_2, as well as other synthetic methods. So the first part studies the selectivity of the ionic liquids. In previous reports, some ionic liquids such as [C_4mim]$ZnCl_3$, [C_4mim]HCO_3, and [C_4mim][OAc] were used as catalysts for the glycolysis and the molecular structure of these ionic liquids were asymmetrical. In our case, the symmetrical stable ionic liquid 1,3-dibutylimidazolium acetate, with alkyl N-substituents, and 1,3-dibenzylimidazolium chloride, with aryl N-substituents, were used. Both ionic liquids have been described in previous reports and were synthesized using different methods.

(a) The "one-pot" cyclisation method to prepare 1,3-dibutylimidazolium acetate.

This method was presented by Zimmermann[78] in 2010 where the 1,3-dibutylimidazolium acetate was synthesized from formaldehyde, butylamine, glyoxal, and acetate acid to get 86% yield and above 95% purity of product.

(b) The alkylation method to prepare 1,3-dibenzylimidazolium chloride.

This method was modified from Tao's report[80] in 2014 where the 1-benzylimidazole was formed firstly by reaction of 1-methylimidazole, sodium hydride and benzyl chloride. 1,3-Dibenzylimidazolium chloride was then synthesized from the formed 1-benzylimidazole and benzyl chloride.

After the desired ionic liquids were generated, the next step was the formation of the carbene and the carboxylate from carbene and CO_2. In Earle's patent[79], the formation of imidazole carbenes was carried out using the apparatus Kugelrohr at high temperature and high pressure. In addition, the method of

the formation of the imidazole carbenes was modified through Duong's report[76]. In this method, the ionic liquid reacted with sodium hydride in THF under nitrogen atmosphere.

After a period of experiments, the above two methods for the carbene formation failed, so another synthesis of carboxylate was applied according to Voutchkova's report[81] where 1-methylimidazole was reacted with dimethyl carbonate (DMC) to directly produce the carboxylate 1,3-dimethylimidazolium-2-carboxylate. After that, the formed carboxylate was used as catalyst for the glycolysis to test the effect of reaction conditions (reaction temperature, reaction time, weight ratio of PET:EG, weight ratio of PET:catalyst) on the conversion of PET, the yield of BHET, and the selectivity of BHET. The obtained results were compared with those of ionic liquid 1,3-dimethylimidazolium acetate which was produced according to the method of 1,3-dibutylimidazolium acetate.

3.2 The synthesis of ionic liquid

3.2.1 1,3-dibutylimidazolium acetate

The ^{1}H NMR spectrum in $CDCl_3$ is shown in **Fig. 2.2.** There are seven different types of hydrogen that integrate with a 1:2:4:3:4:4:6 ratio. The signal at δ 11.49 ppm which doesn't exist in the NMR of any reactants proves the presence of C2-H of the desired product 1,3-dibutylimidazolium acetate.

The signal at δ 7.11 ppm is characteristic of the CH-CH proton of the imidazolium ring, and signals at δ 4.35, 1.85, and 1.37 ppm are characteristic of three types methylene protons of CH_2. The signal at δ 0.94 ppm is the characteristic of the methyl CH_3. And eight different types of carbon in **Fig. 2.3** ^{13}C NMR also proves the formation of product. It is noting that acidic and sensitive proton C2-H signal at δ 11.49 ppm in **Fig. 2.2** and signal at δ 8.52 ppm in **Fig.2.3** are different in chemical shift which depends on the type of solvent used for NMR spectra.[82]

3.2.2 1,3-dimethylimidazolium acetate

The ^{1}H NMR spectrum of 1,3-dimethylimidazolium acetate in D_2O is shown in **Fig. 2.5** indicating the four different types of hydrogen present in the salt, with a 1:2:6:3 integration ratio. The signal at δ 8.52 ppm which doesn't exist in NMR of any reactants proves the presence of C2-H of the desired product 1,3-dimethylimidazolium acetate. Signal at δ 7.29 ppm is characteristic of the CH-CH proton in imidazolium ring. The signal at δ 3.75 ppm is characteristic of the methyl group on N-substituent. The corresponding ^{13}C NMR spectrum (**Fig. 2.6**) contains five different types of carbon environments, also consistent with the formation of the desired product with the presence of only small amount of impurities.

3.2.3 1,3-dibenzylimidazolium chloride

^{1}H-NMR and ^{13}C NMR spectra of the product are shown in **Fig. 2.8** and **Fig. 2.9**. The signals at δ 7.39-7.47 ppm in the ^{1}H NMR spectrum indicate the presence of the ten aromatic protons of the benzene ring. The signal at δ 9.66 ppm is characteristic of the active proton of C2-H (N-CH-N). Signals at δ 7.89 and 5.48 ppm are characteristic of the CH proton in the imidazolium ring and methylene protons of CH_2-benzene ring, and five different types of carbons in the ^{13}C NMR spectrum also prove the formation of the product 1,3-dibenzylimidazolium chloride.

3.3 Synthesis of 1,3-dialkylimidazolium-2-carboxyalte zwitterions

3.3.1 1,3-dimethylimidazolium-2-carboxylate

^{1}H-NMR and ^{13}C NMR spectra of the product are shown in **Fig. 2.11** and **Fig. 2.12.** There are two different types of hydrogen (with a 2:6 integral ratio). The signals at δ 7.28 and 3.90 ppm are characteristic of the CH on the imidazolium ring and methyl CH_3 in N-substituent. The signal at δ 158.60 ppm in the ^{13}C NMR spectra illustrates the presence of carbonyl C=O. All these results shown in spectra prove the formation of the product 1,3-dimethylimidazolium-2-carboxylate.

Fig. 3.1 shows the decarboxylation/decomposition temperature of 1,3-dimethylimidazolium-2-carboxylate. It is obvious that this compound decarboxylated at 160 ^{o}C, where CO_2 escaped from the molecule and free carbenes are released. After that, the residue started to decompose in the process of elevating temperature. So the decarboxylation temperature 160 ^{o}C was selected as initial reaction temperature for the glycolysis of PET.

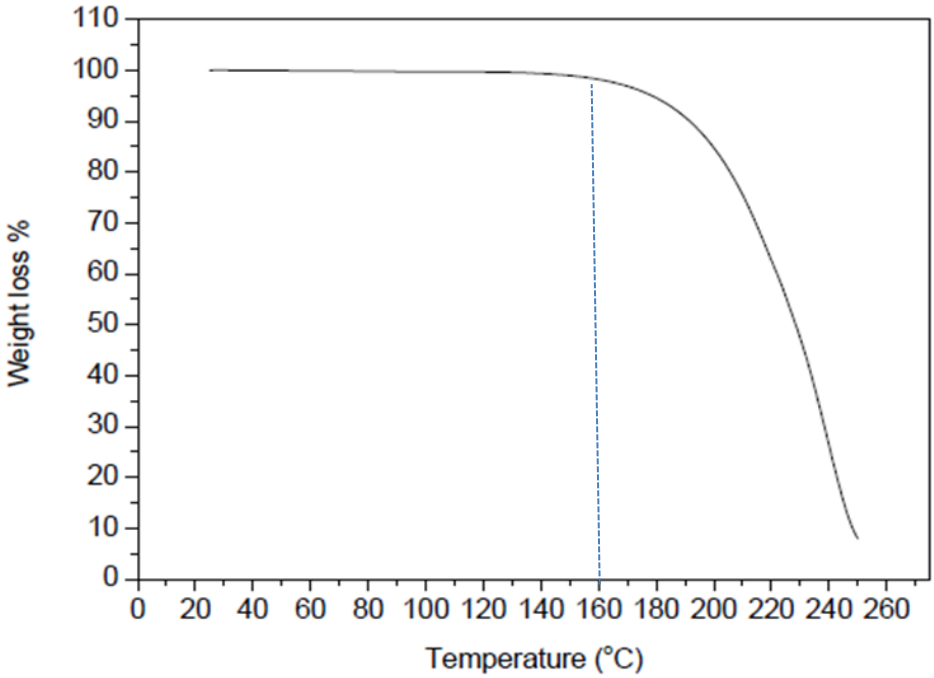
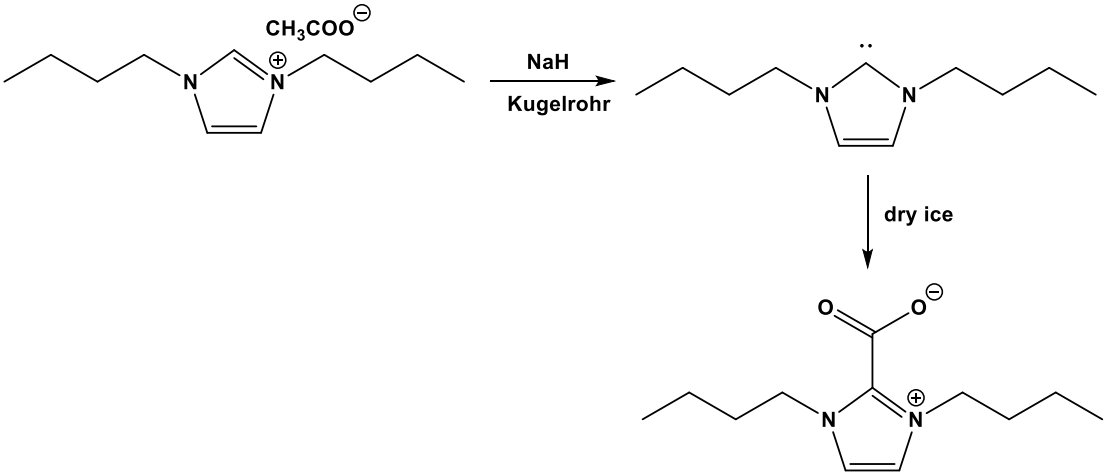


Fig. 3.1 The TGA of 1,3-dimethylimidazolium-2-carboxylate.

3.3.2 1,3-dibutylimidazolium-2-carboxylate

The synthesis of 1,4-dibutylimidazolium-2-carboxylate via intermediate carbene generation followed by reaction with CO_2 was attempted. The C(2)-H deprotonation of 1,3-dibutylimidazolium acetate with base was performed in a Kugelrohr, with distillation of the carbene product from the reaction mixture. Before dry ice was loaded into the tube, a yellow oil was formed and the reactants turned dark from yellow. After dry ice was charged into the flask for the allowed time, there was no change. It is difficult to collect the yellow oil and to do some analytical measurements. There are three possible reasons accounting for this phenomenon. First, the desired carbene wasn't formed. Second, the dry ice was not enough dry, the water from dry ice reacted with the formed carbene forming the imidazolium salt again. Third, with acetate, acetic acid could be formed and distilled from the reaction mixture and then reacted with the carbene.



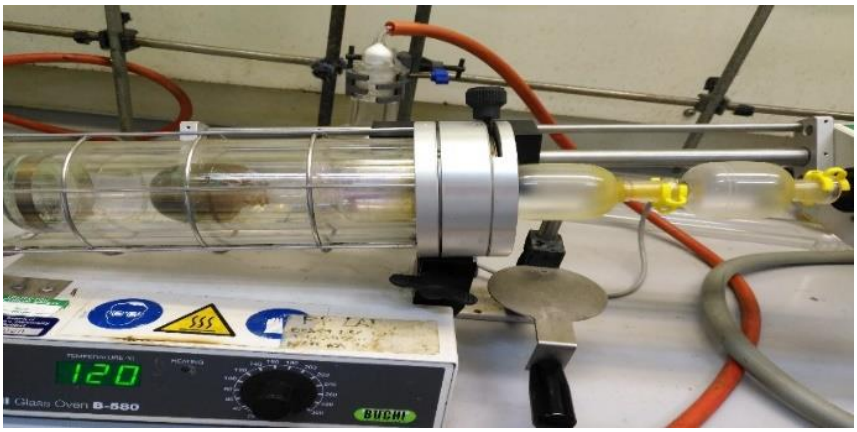
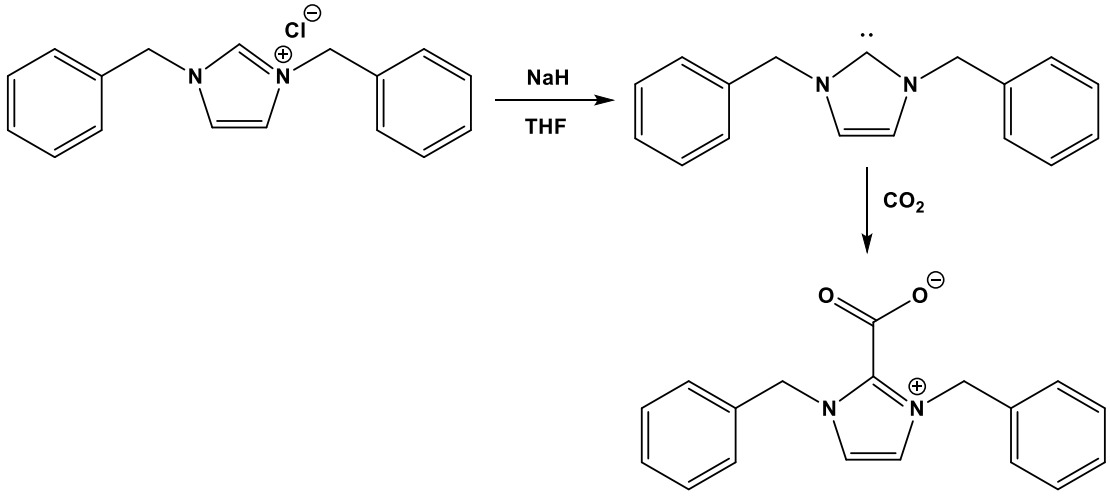


Fig. 3.2 The apparatus for the synthesis of carboxylate.

3.3.3 1,3-dibenzylimidazolium-2-carboxylate

According to the observation, when the ionic liquid 1,3-dibenzylimidazolium chloride reacted with NaH in THF, the oil ionic liquid became powdery and the color of the reaction solution deepened from colorless to red as the reaction time extended. It can be inferred that the chemical reaction was proceeding and some red chemical substance formed. When the red solution was exposed to the air, it turned to light yellow immediately, which indicates that the

substance formed is extremely reactive to the air. As carbene is a very reactive species, it adds the possibility that the desired carbene formed in the reaction. Other than this, the same color change was observed once CO_2 was introduced to react with the red chemical substance. If the red substance contains carbene, it is likely that the expected carboxylate reaction happened with CO_2 and some solid product formed. However, there is no solid product. There are two possible reasons accounting for this. First, the desired reaction did not happen. Second, the presence of impurity makes the mixture liquid.



1,3-dibenzylimidazolium-2-carboxylate

3.4 Glycolysis of PET

3.4.1 The characterization of the main product BHET

In **Fig. 2.16**, the ^1H NMR spectrum of BHET shows the presence of the four different types of hydrogen environments with integral ratios of 4:2:4:4, from the aromatic terephthalate ring (4H, two -CH_2 groups on ethylene glycol substituents, and the terminal glycol OHs). The signal at δ 5.02 ppm is the characteristic of hydroxyl protons of OH which cannot be found in raw material PET. The signals at δ 8.17 ppm indicate the presence of the four aromatic

protons of the benzene ring. And signals at δ 4.39 and 3.78 are the characteristic of methylene protons of CH_2. In **Fig. 2.17** ^{13}C NMR spectra, the signal δ 165.63 ppm is the characteristic of ester carbon of COO and signals δ 134.47 and 129.71 ppm are the characteristic of aromatic carbons of the benzene ring. All these results prove the generation of the product monomer BHET.

The ES-MS spectrum in **Fig. 3.3** shows that the peak up to *m/e* 277 with intensity almost 100% was obtained. This peak is related to the product ionized by Na^+. Thus, molecular weight of the main product is 254 g/mol, which is the same as the molecular weight of BHET.

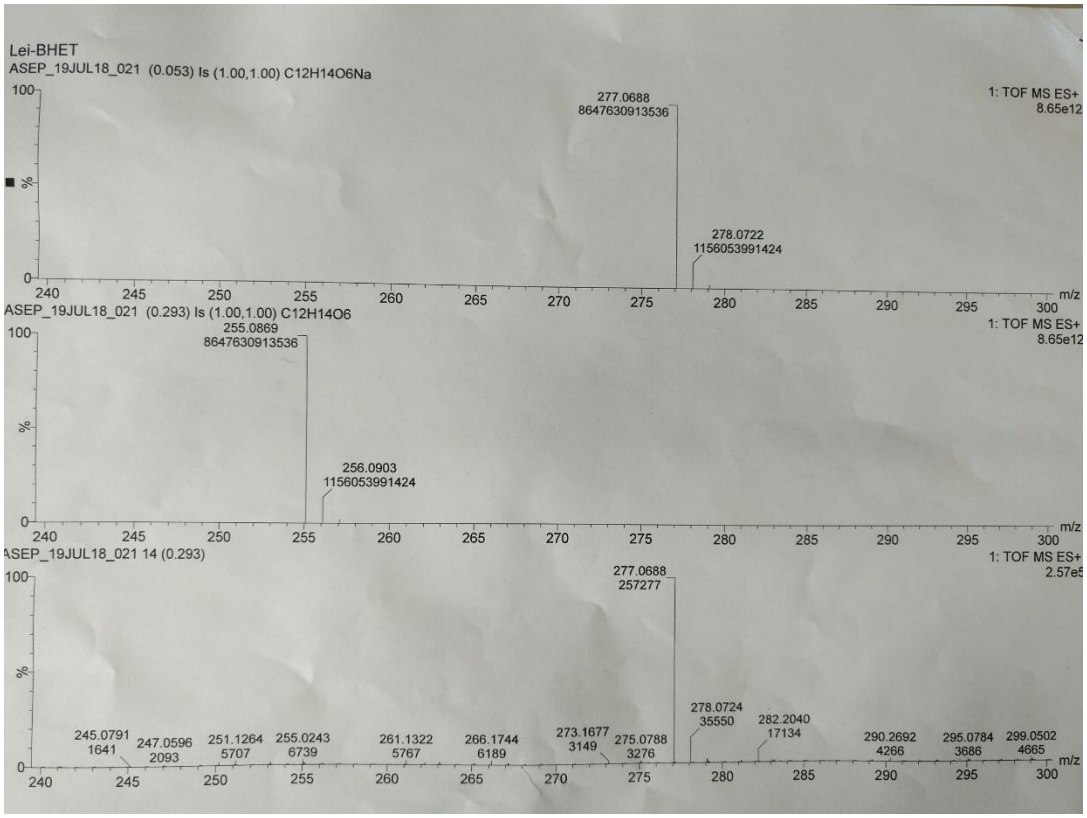


Fig. 3.3 ES-MS of BHET.

There are two TGA curves in **Fig. 3.4** both of which indicate a weight loss from 400 ^{o}C to 450 ^{o}C. The TGA curve of recycled PET without the glycolysis reaction showed only one sharp weight loss starting at 400 ^{o}C which is attributed to the thermal degradation temperature of PET (approximately 400-450 ^{o}C). In contrast, the TGA curve of the glycolysis main product, BHET monomer, has two clear weight losses. The first loss is about 30% starting from 200 ^{o}C which is attributed to the thermal degradation of BHET monomer. With the increasing temperature in TGA, there was a trend that BHET monomer can be repolymerized into PET, so, another weight loss is of about 60% at a starting temperature of 400 ^{o}C due to the thermal degradation of the PET produced by the thermal polymerization of BHET during the thermogravimetric analysis process.[83]

FTIR spectra of PET and BHET was shown in **Fig. 3.5**. An intense broad band between 3200 cm^{-1} and 3600 cm^{-1} can be assigned to the stretching vibration of the hydroxyl group.[84] The ester carbonyl group stretching vibration band is at 1714 cm^{-1}. Alkyl C-H stretching vibration band is at 2954 cm^{-1}, aromatic C-H vibration band is at 1411 cm^{-1}, and 1140 cm^{-1} represents C-O stretching vibration.[85] All stretching vibration bands shown in the figure are all present in BHET.

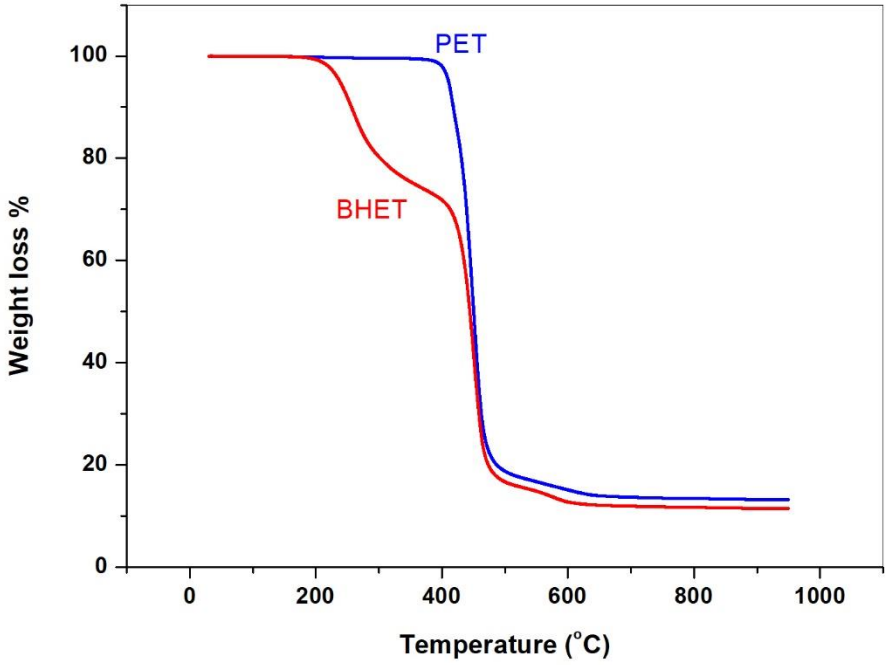


Fig. 3.4 TGA of PET and BHET.

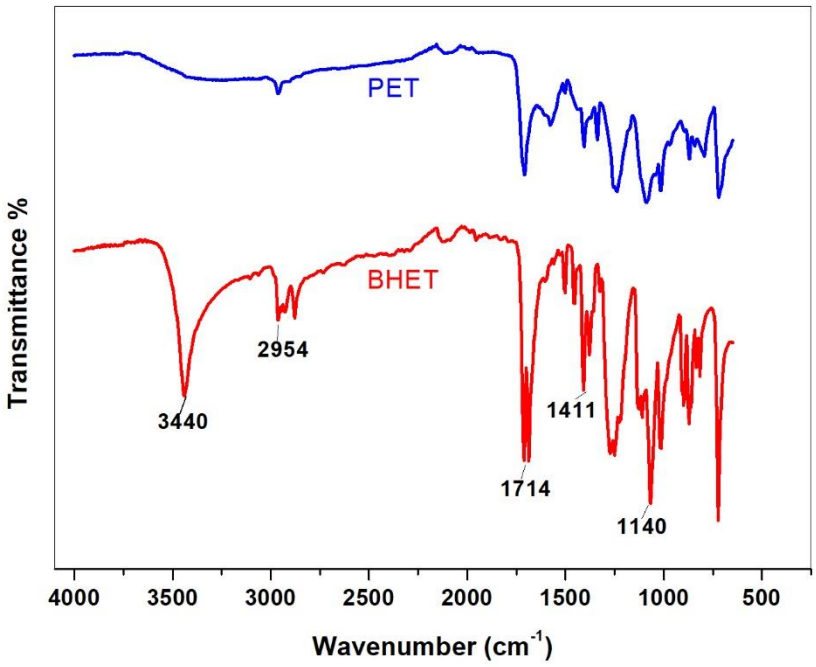


Fig. 3.5 FTIR spectra of BHET and PET.

Fig. 3.6 showed a typical HPLC chromatogram of the glycolysis main product. There was one dominant peak at the retention time of 5.9 min, which is BHET monomer.

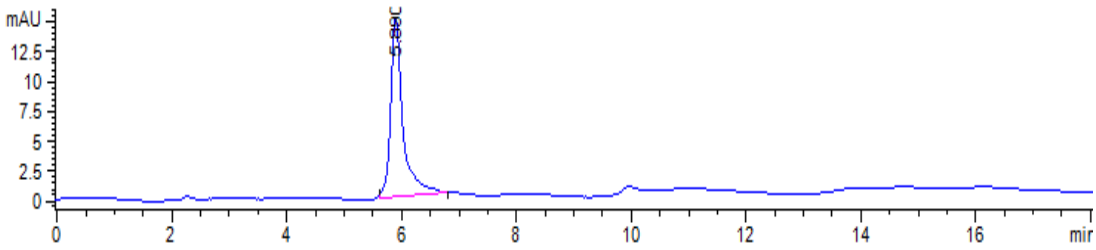


Fig. 3.6 HPLC chromatogram of the glycolysis main product BHET.

A typical HPLC graph of the remaining filtrate after first precipitation of BHET is shown in **Fig. 3.7**. This chromatogram consists of four peaks. The largest signal corresponds to BHET monomer present in the filtrate (at 6.0 min). The peaks with longer elution times, at 9.0 min and 18.8 min correspond to the formation of BHET dimer (9.0 min) and a higher soluble oligomer (18.8 min), which is presumably the trimer. The first peak at 2.6 min is related to the catalyst.

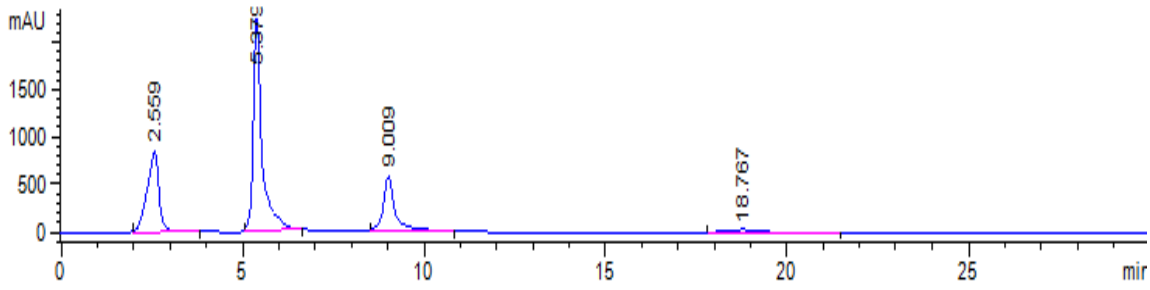


Fig. 3.7 HPLC chromatogram of the remaining filtrate after first precipitation of BHET.

3.4.2 Effect of reaction conditions

The effects of reaction conditions (reaction temperature, reaction time, weight ratio of PET:EG, weight ratio of PET:catalyst) on isolated yield of BHET, conversion of PET, and isolated selectivity of BHET were investigated using two different catalysts 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate ionic liquid.

3.4.2.1 Effect of reaction temperature

The effects of reaction temperature on isolated yield of BHET, conversion of PET, and isolated selectivity of BHET were investigated using two different catalysts 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate ionic liquid.

a. 1,3-dimethylimidazolium-2-carboxylate as catalyst

The **Table 3.1** and **Fig. 3.8** reveal that the isolated yield of BHET, conversion of PET, and isolated selectivity of PET were greatly enhanced with increasing reaction temperature from 160 ^{o}C to 180 ^{o}C when using 1,3-dimethylimidazolium-2-carboxylate as catalyst in the glycolysis of PET. When the temperature was 160 ^{o}C, the PET conversion was only 29%, and there is no isolated BHET yield and no isolated BHET selectivity. However, with increasing glycolysis temperature, the conversion of PET increased drastically up to the maximum value of 100% at 185 ^{o}C. Furthermore, the isolated yield of BHET and the isolated selectivity of BHET increased markedly from 170 ^{o}C to 180 ^{o}C which reached maximum values of 48% and 52.9%, respectively. And then it finally reached certain equilibrium values. Therefore, the glycolysis temperature is very critical for the reaction and 185 ^{o}C is the best temperature for this reaction to obtain 100% PET conversion and higher BHET yield and

BHET selectivity.

Table 3.1[a] Effect of reaction temperature on the glycolysis of PET.

(1 atm, 1.0 g PET, 10.0 g EG, 0.2 g C_1mim-CO_2, 1 h, 255 rpm)

Temperature (°C)	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
160	0	29.0	0
170	0	50.5	0
180	48.0	92.0	52.9
185	48.5	100	48.5
190	49.9	100	49.9
195	50.7	100	50.7
200	50.6	100	50.6

a. The numbers given in the **Table 3.1** are average values.

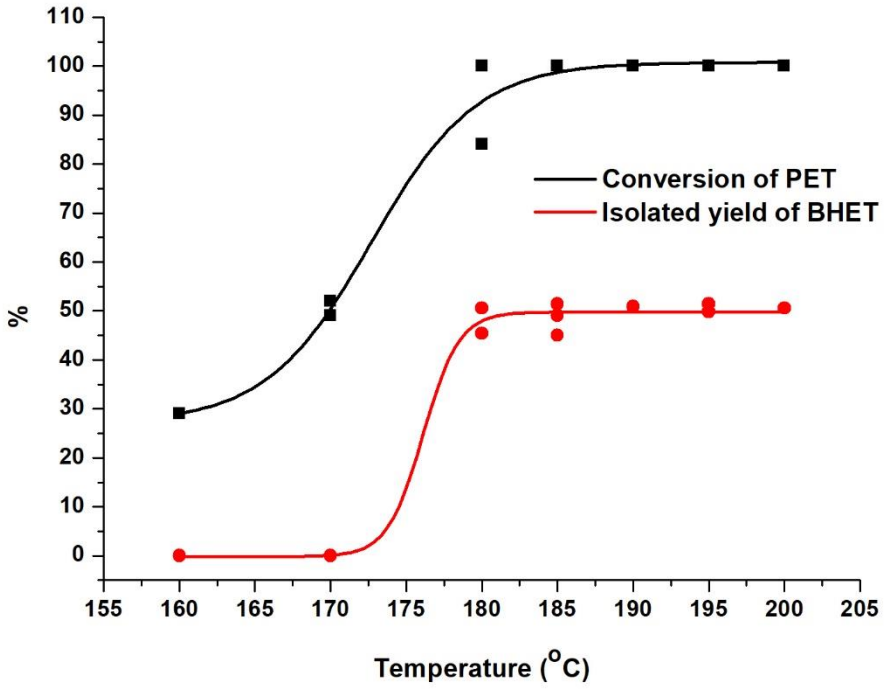


Fig. 3.8 Effect of reaction temperature on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 10.0 g EG, 0.2 g C_1mim-CO_2, 1 h, 255 rpm).

b. 1,3-dimethylimidazolium acetate as catalyst

The effects of reaction temperature of 1,3-dimethylimidazolium acetate ionic liquid as catalyst on the isolated yield of BHET, conversion of PET, and the isolated selectivity of BHET are shown in **Table 3.2** and **Fig. 3.9** by contrast with 1,3-dimethylimidazolium-2-carboxylate. At the same conditions (1 atm, 1.0 g PET, 10.0 g EG, 0.2 g catalyst, 255 rpm, 1 h), from 160 ^{o}C to 180 ^{o}C, there was no isolated BHET yield and no isolated BHET selectivity. At 185 ^{o}C, the isolated BHET yield was only 11.1% which is much lower than 48.5% when the carboxylate was the catalyst. With the increasing temperature, these three values increased gradually and then reached equilibrium. 195 ^{o}C is the best temperature for this reaction to obtain 63.5% PET conversion and 23.8% BHET yield.

Table 3.2[b] Effect of reaction temperature on the glycolysis of PET.

(1 atm, 1.0 g PET, 10.0 g EG, 0.2 g [C_1mim][OAc], 1 h, 255 rpm)

Temperature (^{o}C)	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
160	0	0	0
170	0	0	0
180	0	18.5	0
185	11.1	35.3	31.6
190	18.9	57.0	33.2
195	23.8	63.5	37.5
200	24.2	63.0	38.4

b. The numbers given in the **Table 3.2** are average values.

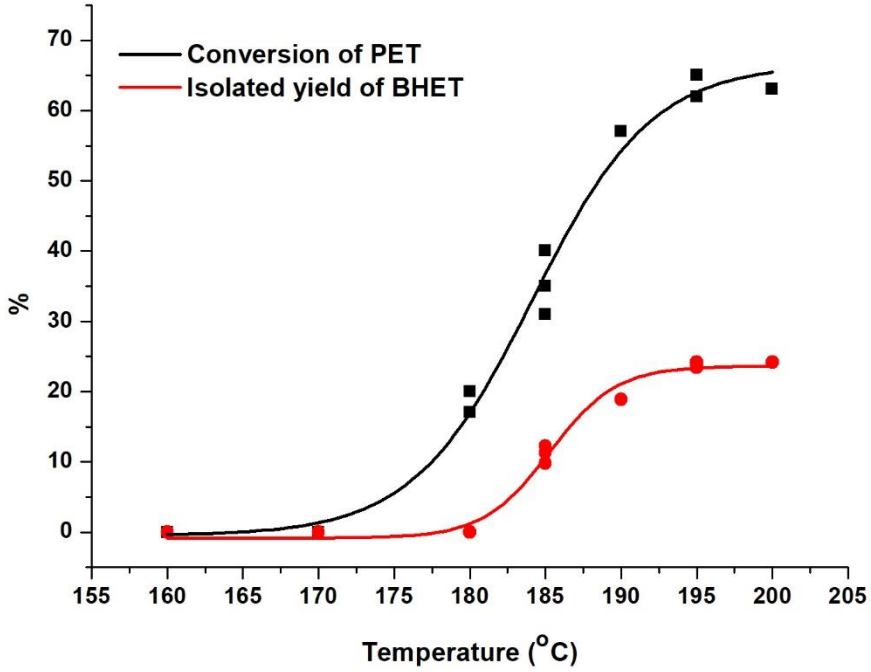


Fig. 3.9 Effect of reaction temperature on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 10.0 g EG, 0.2 g [C_1mim][OAc], 1 h, 255 rpm).

In some reports of glycolysis using different catalysts on the effect of reaction temperature, Al-Sabagh et al.[54] used 1-butyl-3-methylimidazolium acetate ([C_4mim][OAc]) as catalyst for the glycolysis of PET to get 100% PET conversion at 190 °C and maximum value of BHET yield of 46.4%. In 2011, Yue et al[50] presented that using [C_4mim]OH as catalyst for the degradation of PET can obtain 100% PET conversion and above 60% BHET yield at 190 °C. Wang et al.[34] used [C_1mim][$ZnCl_3$] as catalyst for PET degradation to obtain 100% PET conversion and 80.1% BHET selectivity at 175 °C. Yue et al.[51] used [C_4mim]$ZnCl_3$ or [C_4mim]$MnCl_3$ as catalyst to get 100% conversion of PET and above 80% BHET yield at 190 °C. When zinc acetate ($Zn(Ac)_2$) and sodium carbonate (Na_2CO_3) were catalysts in the glycolysis, 196 °C was the best temperature to achieve the complete PET degradation (100% PET

conversion).[32c, 41] Similarly, Pingale[86] used metal salts $ZnCl_2$, LiCl and $MgCl_2$ to achieve above 60% BHET yield at 197 ^oC.

In conclusion, reaction temperature is an important factor for the glycolysis to get higher conversion of PET and higher yield of BHET. Compared with 1,3-dimetylimidazolium acetate ionic liquid, 1,3-dimethylimidazolium-2-carboxylate as catalyst is more effective on the effect of reaction temperature.

3.4.2.2 Effect of reaction time

The effects of reaction time on the isolated yield of BHET, conversion of PET, and isolated selectivity of BHET were examined using two different catalysts 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate ionic liquid.

a. 1,3-dimethylimidazolium-2-carboxylate as catalyst

In **Table 3.3** and **Fig. 3.10**, it is obvious that isolated yield of BHET, conversion of PET, and isolated selectivity of BHET increased with increasing time from 0.5 h to 1 h. When the reaction time was extended to 1 h, the PET conversion was 100%. Moreover, after 1 h, the values of isolated BHET yield and isolated selectivity reached equilibrium. The maximum values of isolated BHET yield and BHET selectivity were 52.2% and 52.2%, respectively. Consequently, 1 h was selected for this carboxylate as the optimum reaction time where the highest PET conversion and higher BHET yield were attained. Thereafter they remained almost constant.

Table 3.3[c] Effect of reaction time on the glycolysis of PET.

(1 atm, 1.0 g PET, 10.0 g EG, 185 ºC, 0.2 g C_1mim-CO_2, 255 rpm)

Reaction Time (h)	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
0.5	30.2	71.5	42.3
1	48.5	100	48.5
2	49.9	100	49.9
3	52.2	100	52.2
4	51.8	100	51.8

c. The numbers given in the **Table 3.3** are average values.

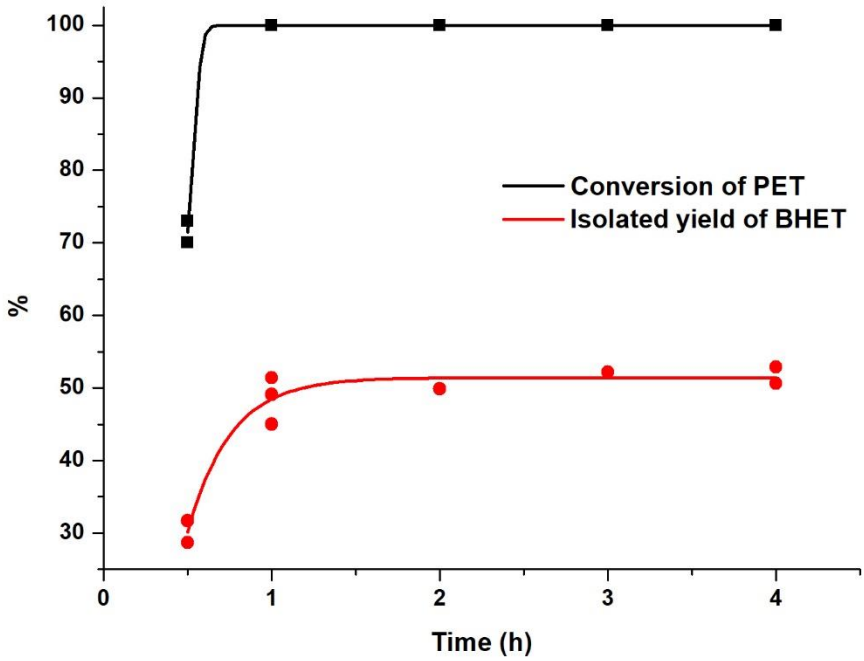


Fig. 3.10 Effect of reaction time on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 10.0 g EG, 185 ºC, 0.2 g C_1mim-CO_2, 255 rpm).

b. 1,3-dimethylimidazolium acetate as catalyst

In the case of the catalyst was 1,3-dimethylimidazolium acetate (**Table 3.4** and **Fig. 3.11)**, the overall trends with increasing reaction time were similar to these of the carboxylate as catalyst. However, the difference is that it required more time (3 h) to obtain 100% PET conversion and higher BHET yield (> 40%) which is close to the 52.2% BHET yield above when the carboxylate was catalyst in the glycolysis of PET.

Table 3.4[d] Effect of reaction time on the glycolysis of PET.

(1 atm, 1.0 g PET, 10.0 g EG, 185 ^{o}C, 0.2 g [C_1mim][OAc], 255 rpm)

Reaction Time (h)	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
0.5	0	10	0
1	11.1	35.3	31.6
2	34.8	79	43.9
3	42.3	100	42.3
4	43.1	100	43.1

d. The numbers given in the **Table 3.4** are average values.

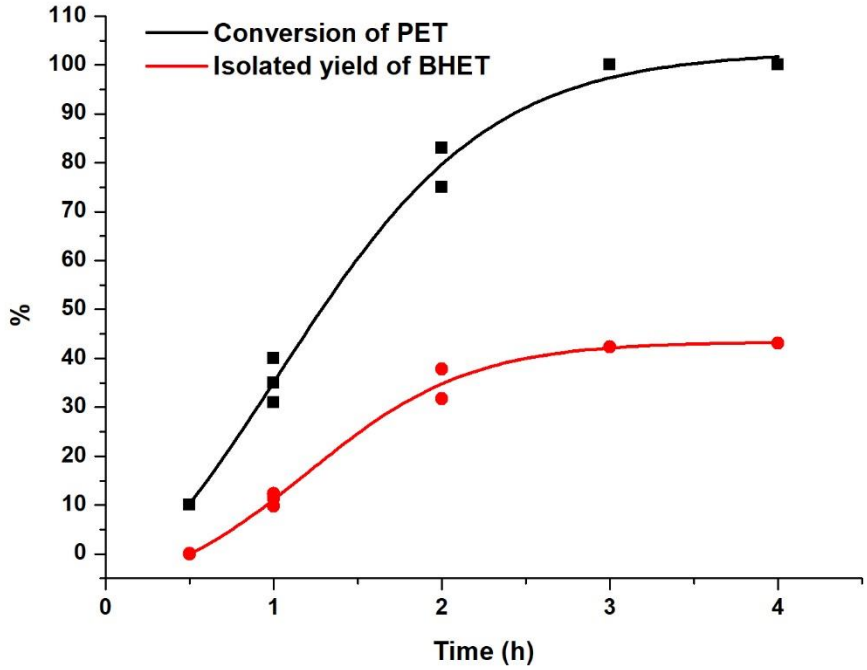


Fig. 3.11 Effect of reaction time on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 10.0 g EG, 185 °C, 0.2 g [C_1mim][OAc], 255 rpm).

However, in the presence of zinc acetate ($Zn(Ac)_2$) or sodium carbonate (Na_2CO_3) as catalyst in the glycolysis of PET, the BHET yield increased significantly from starting to 1 h and then reached equilibrium, and PET conversion attained the maximum value at 1 h.[32c, 41] In Al-Sabagh's report[54] where 1-butyl-3-methylimizolium acetate ([C_4mim][OAc]) was used as catalyst, the PET conversion was 100% when the reaction time was extended to 2 h and the selectivity and yield of BHET reached maximum values when the reaction time was set at 3 h. In Wang's study[34], they required 1.25 h to get 100% PET conversion and 80.1% BHET selectivity when using [C_1mim][$ZnCl_3$]. In addition, [C_4mim]$ZnCl_3$ and [C_4mim]$MnCl_3$ were catalysts for the glycolysis to get 100% conversion of PET and above 80% yield of BHET for just 2 h.[51] However, when using metal salts $ZnCl_2$, LiCl and $MgCl_2$ as catalysts for a long

time 8 h, above 60% yield of BHET was obtained.[86]

As a result, reaction time as an important factor can affect the conversion of PET and yield of BHET. 1,3-dimethylimidaolium-2-carboxylate can catalyze more quickly than ionic liquid 1,3-dimethylimidazolium acetate in the reaction time.

3.4.2.3 Effect of weight ratio of PET:EG

The effects of the weight ratio of PET:EG on the isolated yield of BHET, conversion of PET, and isolated selectivity of BHET were examined using two different catalysts 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate ionic liquid.

a. 1,3-dimethylimidazolium-2-carboxylate as catalyst

The ethylene glycol dosage has an important impact on the isolated yield of BHET, conversion of PET, and isolated selectivity of BHET. As shown in **Table 3.5** and **Fig. 3.12**, under the conditions of 0.2 g catalyst, a reaction temperature of 185 ^{o}C, 1.0 g PET, and 1 h reaction time, the isolated yield of BHET, isolated selectivity of BHET, and conversion of PET reached maximum values 48.5%, 48.5%, and 100% respectively, at an ethylene glycol dosage of 10 g. The isolated yield of BHET and the isolated selectivity of BHET decreased with the dosage of ethylene glycol growing, at PET:EG ratio 1:12.5, 1:15, and 1:20, respectively. When the dosage of ethylene glycol was 20 g, the isolated yield of BHET decreased to 22.7%. It may be attributed to the decrease of catalytic consistence when we increased or decreased value of PET:EG ratio. In other words, too much ethylene glycol or too less ethylene glycol with a certain amount of catalyst can influence the formation of BHET. And with less ethylene glycol, it should be possible to precipitate most of the BHET on cooling, and

then the excess ethylene glycol or catalyst liquid could be recycled directly. It is interesting that the PET conversions were all 100% from PET:EG 1:5 to 1:20, which indicated that under these conditions (185 °C, 1.0 g PET, 0.2 g catalyst, 1 h) and different dosage of ethylene glycol, 1,3-dimethylimidazolium-2-carboxylate has a strong catalytic ability to catalyze from PET to BHET, dimer or higher oligomers.

Table 3.5[e] Effect of weight ratio of PET:EG on the glycolysis of PET.

(1 atm, 1.0 g PET, 185 °C, 0.2 g C_1mim-CO_2, 1 h, 255 rpm)

Weight ratio of PET:EG	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
1:5	15.1	100	15.1
1:7.5	23.6	100	23.6
1:10	48.5	100	48.5
1:12.5	37.1	100	37.1
1:15	31.0	100	31.0
1:20	22.7	100	22.7

e. The numbers given in the **Table 3.5** are average values.

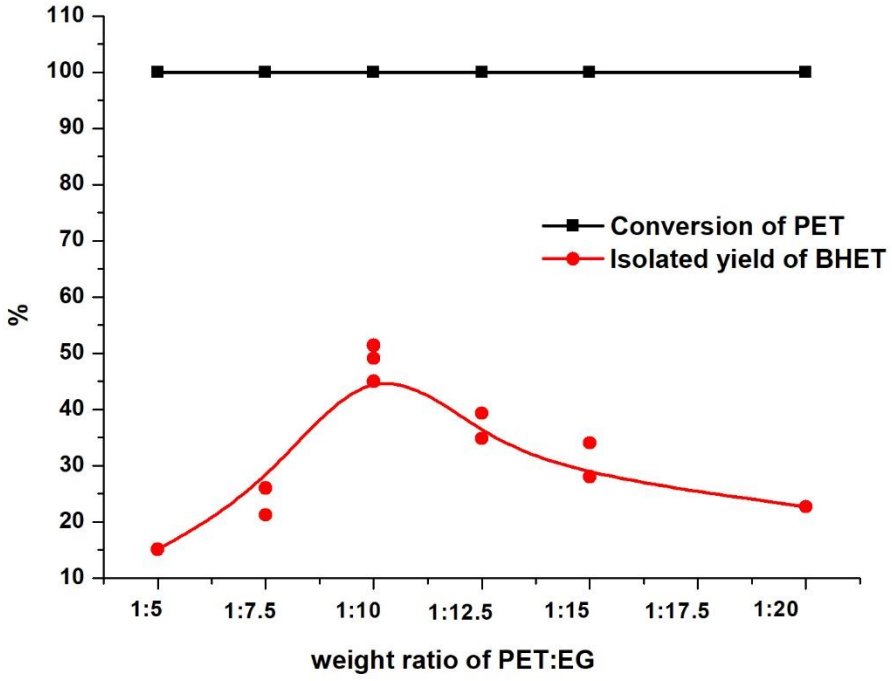


Fig. 3.12 Effect of weight ratio of PET:EG on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 185 ^{o}C, 0.2 g C_1mim-CO_2, 1 h, 255 rpm).

b. 1,3-dimethylimidazolium acetate as catalyst

By contrast, when the acetate ionic liquid was the catalyst as shown in **Table 3.6** and **Fig. 3.13**, the PET conversion, isolated BHET yield, and isolated BHET selectivity all decreased with the increasing ethylene glycol dosage which reveals that the weight ratio PET:EG 1:5 was the most suitable for this catalytic reaction under the condition. It also means that 0.2 g catalyst ionic liquid requires less ethylene glycol to get higher BHET yield and PET conversion when compared with the carboxylate.

Table 3.6[f] Effect of weight ratio of PET:EG on the glycolysis of PET

(1 atm, 1.0 g PET, 185 °C, 0.2 g [C_1mim][OAc], 1 h, 255 rpm)

Weight ratio of PET:EG	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
1:5	17.2	38.5	44.6
1:7.5	15.0	37.0	40.5
1:10	11.1	35.3	31.6
1:12.5	10.2	34.5	29.4
1:15	7.3	28.0	25.7
1:20	0	19.0	0

f. The numbers given in the **Table 3.6** are average values.

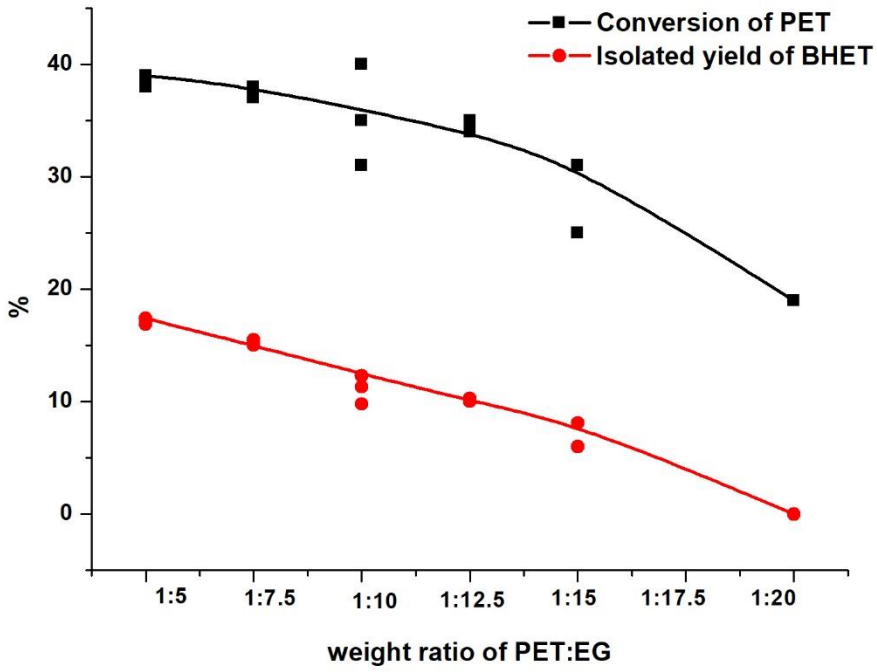


Fig. 3.13 Effect of weight ratio of PET:EG on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 185 °C, 0.2 g [C_1mim][OAc], 1 h, 255 rpm).

There are different results in other reports of glycolysis using different catalysts on the effect of mass ratio of PET:EG. When the zinc acetate ($Zn(Ac)_2$) or sodium carbonate (Na_2CO_3) were used as catalyst in the glycolysis of PET, the yield of BHET grew slowly from the EG:PET molar ratio of 3.8:1 to 7.6:1 and reached the maximum value at EG:PET molar ratio of 7.6:1 where the conversion of PET was 100%.[32c, 41] In Al-Sabagh's report, the conversion of PET, selectivity and yield of BHET reached 100%, 53.5%, and 53.5%, respectively at an EG dosage of 20 g (PET 2 g) when [C_4mim][OAc] catalysed the glycolysis of PET and all of three values (PET conversion, BHET yield, and BHET selectivity) all decreased as the EG dosage was increased to 25 g.[54] When the weight ratio of PET:EG was 5:20 using catalysts [C_4mim][$MnCl_3$] and [C_4mim][$FeCl_4$], about 50% yield of BHET was obtained.[53] 100% PET conversion and above 60% BHET yield were both achieved when using [C_4mim]OH as catalyst with 2 g PET and 20 g ethylene glycol.[50]

By comparing with different catalysts, it is obvious to illustrate that the ethylene glycol dosage is a very important parameter for the glycolysis reaction.

3.4.2.4 Effect of weight ratio of PET: catalyst

The effects of the weight ratio of PET:catalyst on the isolated yield of BHET, conversion of PET, and isolated selectivity of BHET were examined using two different catalysts 1,3-dimethylimidazolium-2-carboxylate and 1,3-dimethylimidazolium acetate ionic liquid.

a. 1,3-dimethylimidazolium-2-carboxylate as catalyst

The effects of weight ratio of PET:catalyst on the isolated yield of BHET, the conversion of PET, and the isolated selectivity of BHET were investigated (**Table 3.7** and **Fig. 3.14**) using catalyst 1,3-dimethylimidazolium-2-carboxylate. The presence of catalyst has an important role in the conversion,

selectivity, and yield in the glycolysis reaction of PET. The conversion of PET, and the isolated yield of BHET increased significantly when the amount of 1,3-dimethylimidazolium-2-carboxylate was added from 0.05 g to 0.15 g. The conversion and yield reached 100%, and 61%, respectively. After that, with the increasing amount of catalyst, the conversion of PET remained at 100%, however, the isolated yield of BHET decreased sharply to 12.1% at 0.4 g. At the same time, the isolated selectivity of BHET decreased as well. This trend is the result of the increase of the catalyst content which speeds up the reaction process. In addition, the presence of large amounts of NHC in the mixture changes the solubility of BHET (NHC can interact with monomer BHET forming hydrogen bonding) and easily keeps the BHET in the reaction solution. This causes it difficult to form or crystal monomer BHET because the molecular weight of catalyst is close to that of BHET.

Table 3.7[g] Effect of weight ratio of PET: catalyst on the glycolysis of PET.

(1 atm, 1.0 g PET, 10.0 g EG, 185 ^{o}C, 1 h, C_1mim-CO_2, 255 rpm)

Weight ratio of PET: catalyst	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
1:0.05	9.1	23	39.4
1:0.1	48.5	86.5	56.1
1:0.15	61.0	100	61.0
1:0.2	48.5	100	48.5
1:0.3	37.5	100	37.5
1:0.4	12.1	100	12.1

g. The numbers given in the **Table 3.7** are average values.

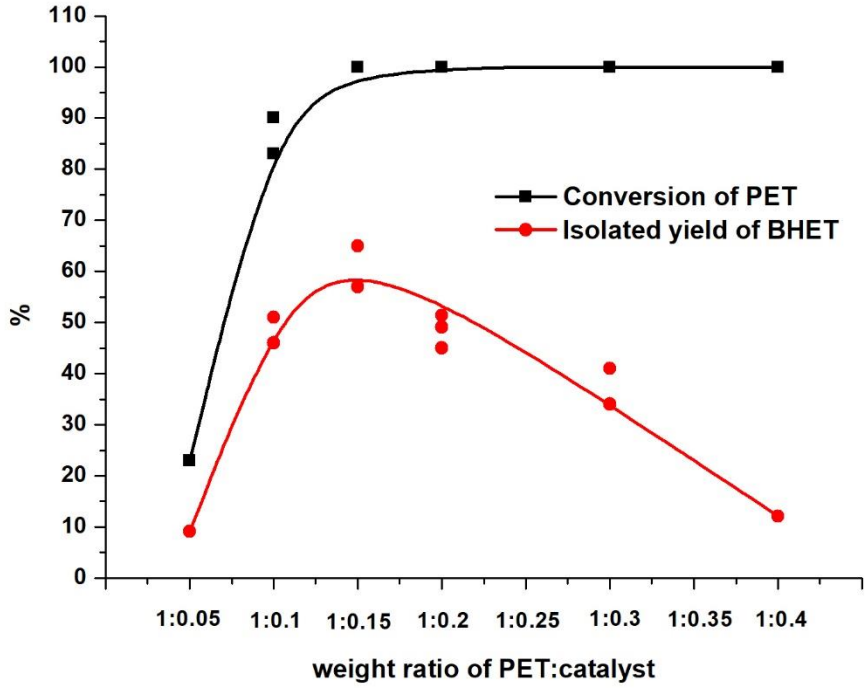


Fig. 3.14 Effect of weight ratio of PET: catalyst on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 10.0 g EG, 185 ^{o}C, 1 h, C_1mim-CO_2, 255 rpm).

b. 1,3-dimethylimidazolium acetate as catalyst

From **Table 3.8** and **Fig. 3.15**, similar trends were observed when the ionic liquid 1,3-dimethylimidazolium acetate was used as the catalyst. The conversion of PET went up gradually when the amount of catalyst increased from 0.05 g to 0.4 g, but the isolated yield of BHET first increased to 14.7% at 0.3 g and then declined to 13.1% at 0.4 g. When more ionic liquid was added, the monomer BHET formed more quickly. The formed BHET in the reaction solution, however, can then polymerize into dimer or higher oligomers, resulting in the decrease of the amount of BHET monomer.[87]

Table 3.8[h] Effect of weight ratio of PET: catalyst on the glycolysis of PET.

(1 atm, 1.0 g PET, 10.0 g EG, 185 °C, 1 h, [C_1mim][OAc], 255 rpm)

Weight ratio of PET: catalyst	Isolated yield of BHET (%)	Conversion of PET (%)	Isolated selectivity of BHET (%)
1:0.05	3.8	9.0	42.0
1:0.1	7.6	19.0	39.8
1:0.15	9.9	24.5	40.8
1:0.2	11.1	35.3	31.6
1:0.3	14.7	38.5	38.5
1:0.4	13.1	47.5	27.5

h. The numbers given in the **Table 3.8** are average values.

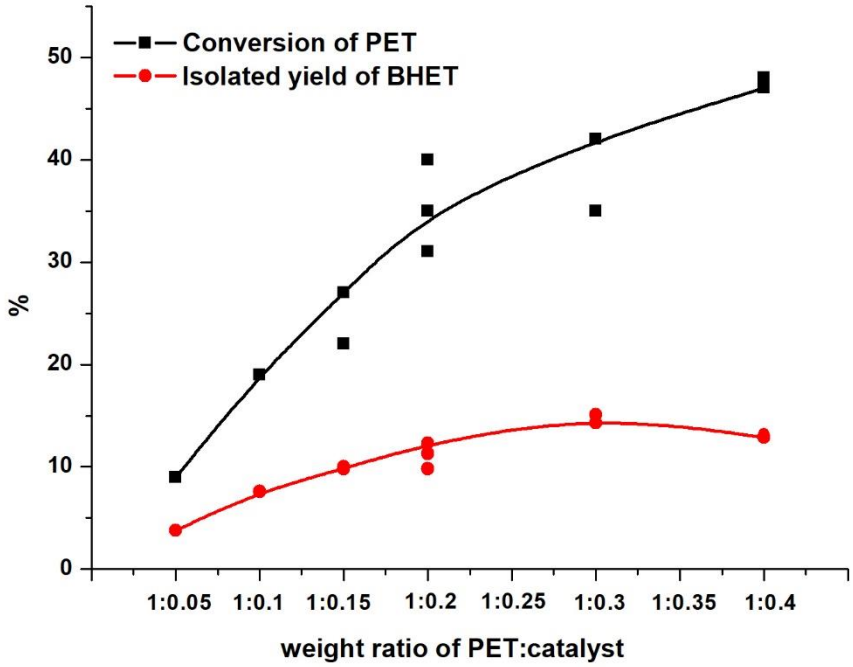


Fig. 3.15 Effect of weight ratio of PET: catalyst on the isolated yield of BHET, the conversion of PET (1 atm, 1.0 g PET, 10.0 g EG, 185 °C, 1 h, [C_1mim][OAc], 255 rpm).

The catalytic performances of various catalysts were studied in the glycolysis reaction of PET in some reports. By contrast, the BHET yield increased with the increasing amount of catalyst $Zn(Ac)_2$ or Na_2CO_3 from 0.25% to 1% (catalyst:PET molar ratio), and it reached the maximum value (about 80%) at 1% load of catalyst.[32c, 41] However, when [C_4mim][OAc] was used as a Lewis base catalyst under the conditions of 20 g EG, 3 g PET, 3 h and 190 ^oC, the PET conversion reached 100% and the BHET yield reached 58.2% at [C_4mim][OAc] of 1 g.[54] Similarly, the 100% PET conversion and 80.1% attained at the 10 wt% (catalyst:PET) loading of [C_1mim][$ZnCl_3$] at 175 ^oC for 1.25 h with PET:EG mass ratio of 1:4.[34] Using less amount of catalyst 1.25 wt% [C_4mim]$ZnCl_3$ or 0.63 wt% (the weight ratio of PET:catalyst) [C_4mim]$MnCl_3$ for the glycolysis can get 100% conversion of PET and above 80% yield of BHET.[51] However, when the amount of catalysts [C_4mim]Cl, [C_4mim]Br, or [C_4mim]HSO_4 was 1 g with 5 g PET, the conversion of PET was just less than 10%.

So the catalyst can increase the rate of glycolysis of PET and the amount of catalyst can affect the conversion of PET, the yield of BHET and the selectivity of BHET. 1,3-dimethylimidazolium-2-carboxylate as catalyst is more reactive than the 1,3-dimethylimidazolium acetate.

When the 1,3-dimethylimidazolium-2-carboxylate was used as the catalyst, at the conditions of 185 ^oC, 1 h, 1 g PET, 10 g ethylene glycol and 0.15 g catalyst, the HPLC graph of the crude reaction mixture (**Fig. 3.16**) shows all BHET still in the supernatant solution after the glycolysis reaction. In the reaction mixture, the concentration of all BHET which shows in 6.9 min in the figure is 120.43 mg/ml. However, when the reaction mixture was stored in a refrigerator at 0 ^oC for 24 h, white crystalline flakes (BHET) were formed, which were separated by filtration and dried. The HPLC chromatogram of the remaining filtrate after the first precipitation of BHET is shown in **Fig. 3.17**. It illustrates that this

remaining filtrate contains ethylene glycol, catalyst, a small part of BHET at 6.9 min in the figure, dimer, and other oligomers. The concentration of remaining BHET in the filtrate is 6.71 mg/ml. It means that a little BHET can be soluble in the filtrate (the solubility of BHET in water is 17.61 mg/ml[88]) and the calculated BHET yield and BHET selectivity do not represent all BHET formed in the glycolysis reaction. At other conditions, after crystallisation of BHET from the reaction mixture in the refrigerator, the remaining solutions contained soluble BHET at 6-10 mg/ml concentration (**Appendix**) which was explained by the solubility of BHET in water.

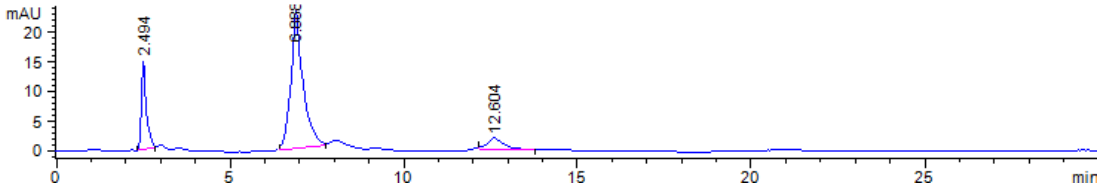


Fig. 3.16 HPLC chromatogram of the crude reaction mixture.

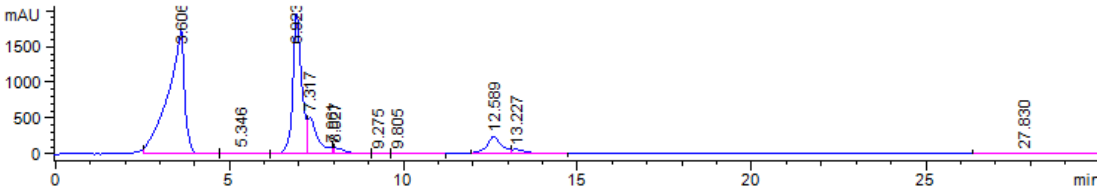


Fig. 3.17 HPLC chromatogram of the remaining filtrate after first precipitation of BHET.

After filtering the crystalline monomer BHET from the reaction mixture, the remaining filtrate was recycled to proceed the glycolysis reaction at the same conditions (185 °C, 1 h，PET:EG 1:10). Finally, 100% PET conversion, 45.4% BHET yield were obtained, which indicated that the filtrate with catalyst can be recycled to get higher PET conversion and BHET yield as well. The similar

results of recycling catalysts have been previously reported. For example, when the catalyst [C_1mim][$ZnCl_3$][34] was recycled in the glycolysis, the degradation efficiency does not reduce in the sixth recycling of catalyst and residual EG which was shown similarly in ionic liquid [C_4mim][OAc][54] as catalyst.

In some reports (shown in **Appendix**), neutral ionic liquid [C_4mim]Cl was used as the catalyst in the glycolysis to obtain 28.9% PET conversion, and 6.0% BHET yield; the basic ionic liquid [C_4mim]HCO_3 was used to get 82.8% PET conversion but 14.1% BHET yield; When the strong basic ionic liquid [C_4mim]OH was the catalyst in the glycolysis, 100% PET conversion and 71.2% BHET yield was obtained under the optimum conditions of the content of catalyst, [C_4mim]OH is 5 wt%, reaction temperature 190 ^oC and time 2 h, weight ratio of PET:EG is 1:10.[50] Similarly, when the basic ionic liquid [C_4mim][OAc] was used as catalyst in the glycolysis, 100% PET conversion and 58.2% BHET yield obtained using 1.0 g catalyst with 2.0 g EG and 3.0 g PET at 190 ^oC for 3 h.[54] The PET conversion and the BHET yield were achieved at 100% and 83.8% respectively with loading acidic ionic liquid [C_4mim]$ZnCl_3$ catalyst at 0.16 wt% at 180 ^oC for 5 h.[51-52] When the metal salt zinc acetate or sodium carbonate was the catalyst for the glycolysis, a yield of BHET close to 70% was obtained at 196 ^oC with an EG:PET molar ratio of 7.6:1 and 1 mol% catalyst.[41] Using different catalysts for the glycolysis can obtain different conversion of PET, yield of BHET and the selectivity of BHET under different conditions (reaction temperature, reaction time, weight ratio of PET:EG, weight ratio of PET:catalyst). So it is difficult to compare and judge which catalyst is better or more efficient for the glycolysis of PET using different conditions.

In this study, when 1,3-dimethylimidazolium-2-carboxylate was used as catalyst for the glycolysis, 100% PET conversion and 61% BHET yield were

obtained with 1.0 g PET, 10.0 g EG, 0.15 g catalyst (15 wt%) at 185 ^{o}C under nitrogen for 1 h which was compared with 1,3-dimethylimidazolium acetate as catalyst to achieve 100% PET conversion and >60% BHET yield with 0.3 g catalyst (30 wt%) at 195 ^{o}C for 3 h.

Comparison between ionic liquid and carboxylate as precursor of carbene can combine with Rodríguez's report which proposed carbene mechanisms in imidazolium-catalysed transesterification reactions. They presented that pure 1,3-diakylimidazolium ionic liquids can be induced to undergo activity transformations via NHCs as both reactant and solvent in the absence of bases by reaction of [C_2mim][OAc] with sulfur or selenium to directly form imidazole-2-chalcogenones and described the equilibrium presence of carbene species in acetate ionic liquid.[89] In Welton's reports, they described the spontaneous formation of N-heterocyclic carbenes in imidazolium based ionic liquid especially acetate ionic liquid and presented the mechanism of carbene catalysis on benzoin condensation where the formation of carbenes by a proton transfer from the cation to the anion.[90] That is why 1,3-dimethylimidazolium-2-carboxylate performed more efficient than the ionic liquid 1,3-dimethylimidazolium acetate. Because when the 1,3-dimethylimidazolium acetate was catalyst for the glycolysis, there was an equilibrium between ionic liquid and carbene. It is still ionic liquid that mainly catalyzed the reaction. However, when the 1,3-dimethylimidazolium-2-carboxylate as catalyst for the glycolysis, the carboxylate decarboxylated at high temperature to release CO2 and make the reaction moving to the direction of generating carbenes. It is carbene that mainly catalyzed the reaction.

Chapter 4

Conclusion

This is the first time that the imidazolium-carboxylate has been used as a catalyst (or catalyst precursor) for the glycolysis of PET. The catalyst 1,3-dimethylimidazolium-2-carboxylate was synthesized easily from the reaction of DMC with 1-methylimidazolium, and it is stable to store and use. In the glycolysis, the main product from the depolymerization catalyzed by carboxylate was monomer BHET. The results showed that reaction parameters, such as reaction temperature, glycolysis time, the ethylene glycol dosage and the amount of catalyst can effect the glycolysis of PET on the yield of BHET, the conversion of PET, and the selectivity of BHET. When the 1,3-dimethylimidazolium-2-carboxylate was used in the glycolysis, complete PET degradation (100% PET conversion) was obtained at 180 ^{o}C, 1 h, with 10 wt% load of catalyst and at 1:5 ratio PET:EG. Using 1.0 g PET, 10.0 g ethylene glycol, 0.15 g catalyst at 185 ^{o}C under nitrogen for 1 h can give the maximum BHET yield (61%), 100% PET conversion, and the higher BHET selectivity. When the ionic liquid 1,3-dimethylimidazolium acetate was used as the catalyst in the glycolysis, it would require longer time (3 h), higher temperature (195 ^{o}C), more catalyst (0.3 g) and the relative ethylene glycol to get > 60% BHET yield, 100% PET conversion. By contrast, it is demonstrated that 1,3-dimethylidazolium-2-carboxylate can behave as a more efficient catalyst than ionic liquid 1,3-dimethylimidazolium acetate for the glycolysis in the presence of ethylene glycol. In addition, the carboxylate catalyst was recycled in the glycolysis which conforms to the principles of sustainable development and performs valuable to further study. As the reported separation of BHET from the reaction mixture was not all the BHET formed in the glycolysis, so further work needs to be done to explore better isolation of BHET and separate the BHET from the remaining reaction mixture to achieve the maximum recycle of BHET.

In term of the synthesis of carbene using Kugelrohr, the reason for the failure is that no high vacuum was possible in the apparatus, the impurity of the reagents (ionic liquid, or dry ice), or the incomplete inert working environment. Similarly, the reason for the failure of another method to synthesize the carboxylate with ionic liquid, sodium hydride, and CO_2 is conjectured to be the impurity of the reagents or the incompletely inert working environment. So, the continuing work will be the attempt to conduct the whole experiment in strict working environment such as glove box to reach the best inert reaction condition.

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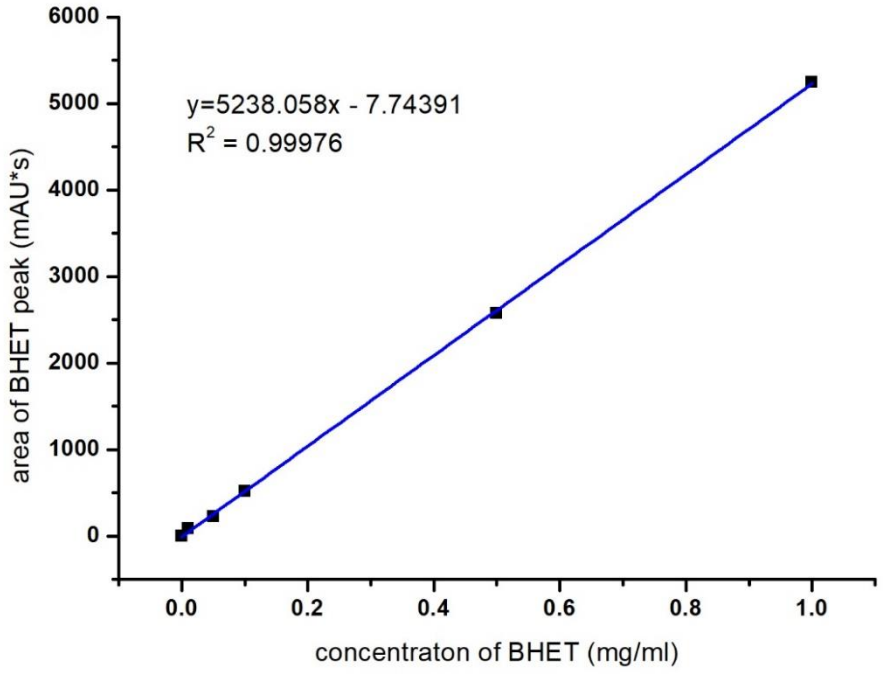
Appendix

Chemicals list

Chemical	Purity	Supplier
Methylamine	40%	Aldrich
Formaldehyde	37%	Alfa Aesar
Acetate acid	99.7%	Sigma-Aldrich
Glyoxal	40%	Sigma-Aldrich
Diethyl ether	≥99.5%	Sigma-Aldrich
Butylamine	99%	Aldrich
Imidazole	≥99%	Aldrich
Tetrahydrofuran	≥99.9%	Sigma-Aldrich
Sodium hydride	60%	Aldrich
Benzyl chloride	99%	Aldrich
1-methylimidazole	≥99%	Sigma-Aldrich
Dimethyl carbonate	99%	Aldrich
Acetone	≥99%	Fisher Chemical
Acetonitrile	≥99.9%	Sigma-Aldrich
Methanol	≥99.8%	Fisher Chemical
Ethylene glycol	99%	SciChem

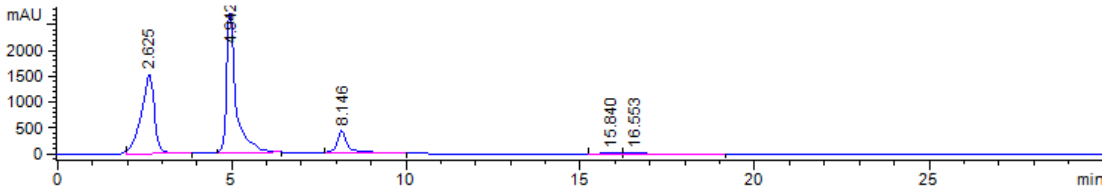
HPLC Results

(1) The calibration of BHET content in the reaction mixture.



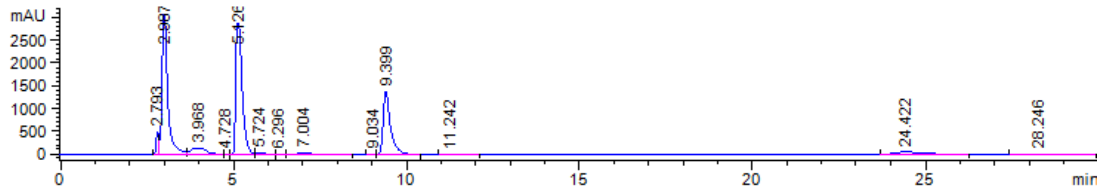
(2) 1,3-dimethylimidazlium-2-carboxylate as catalyst

(a) 185 °C, 1 h, 10.0 g EG, 0.2 g catalyst



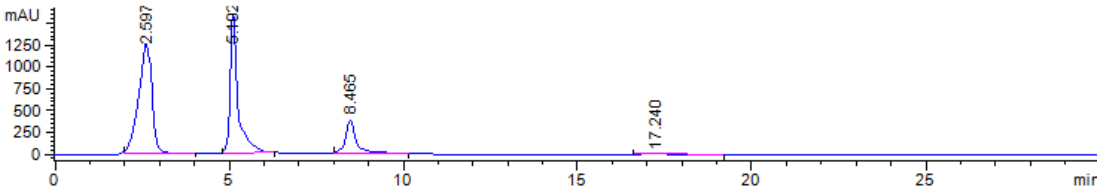
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 9.95 mg/ml.

(b) 185 °C, 0.5 h, 10.0 g EG, 0.2 g catalyst



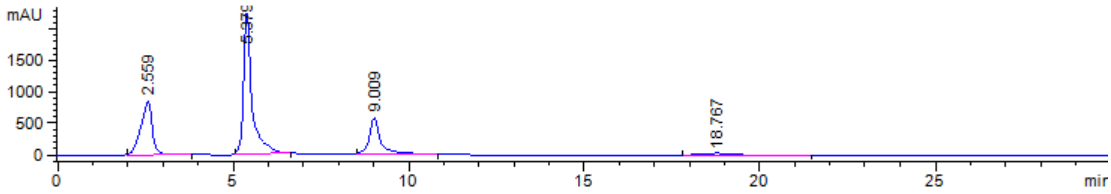
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 7.07 mg/ml.

(c) 185 °C, 1 h, 5.0 g EG, 0.2 g catalyst



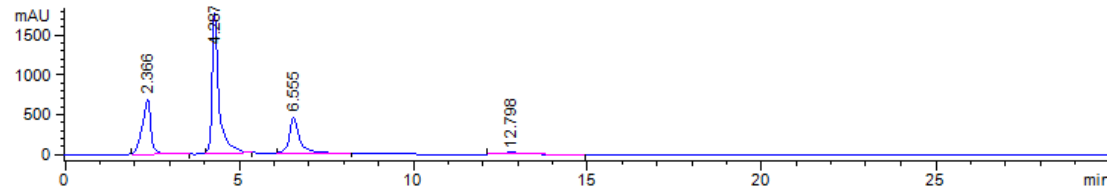
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.88 mg/ml.

(d) 185 °C, 1 h, 20.0 g EG, 0.2 g catalyst



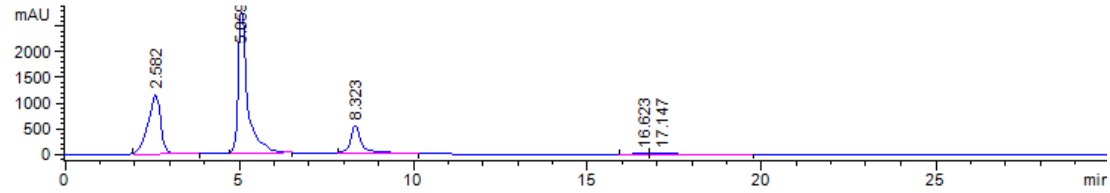
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 7.25 mg/ml.

(e) 185 °C, 1 h, 10.0 g EG, 0.05 g catalyst



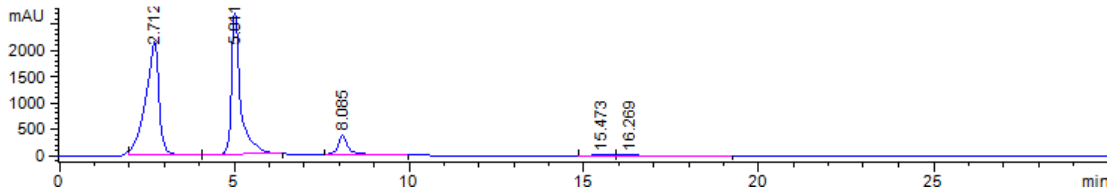
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.70 mg/ml.

(f) 185 °C, 1 h, 10.0 g EG, 0.15 g catalyst



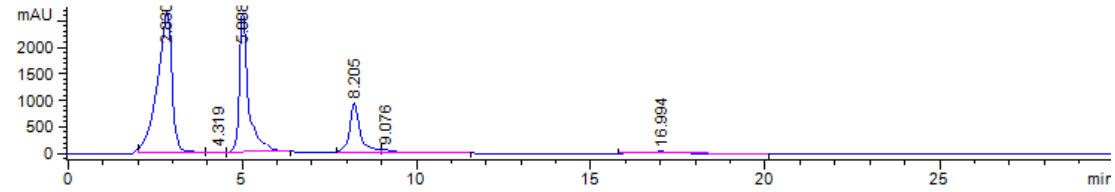
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 10.18 mg/ml.

(g) 185 °C, 1 h, 10.0 g EG, 0.3 g catalyst



After filtering crystal monomer BHET, the content of BHET in reaction mixture is 9.45 mg/ml.

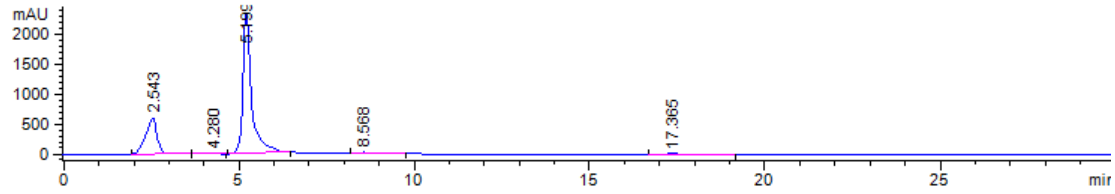
(h) 185 ºC, 1 h, 10.0 g EG, 0.4 g catalyst



After filtering crystal monomer BHET, the content of BHET in reaction Mixture is 9.14 mg/ml.

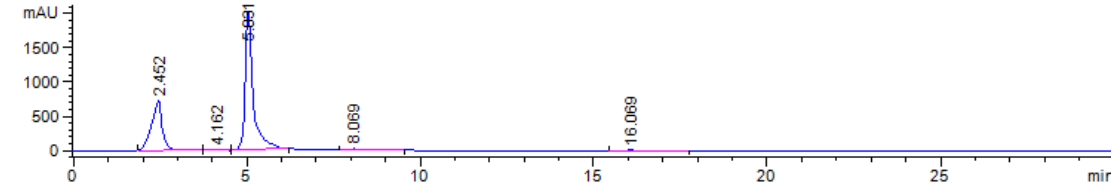
(3) 1,3-dimethylimidazolium based ionic liquid as catalyst

(a) 180 ºC, 1 h, 10.0 g EG, 0.2 g catalyst



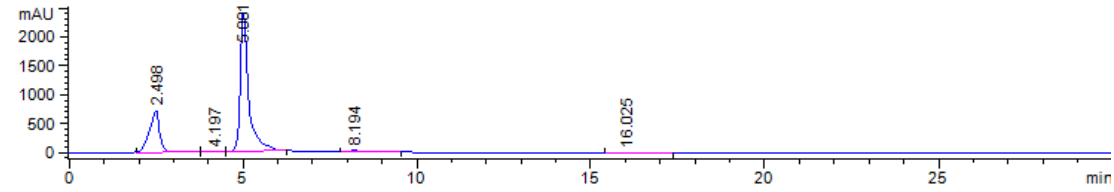
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 7.78 mg/ml.

(b) 185 ºC, 1 h, 10.0 g EG, 0.2 g catalyst



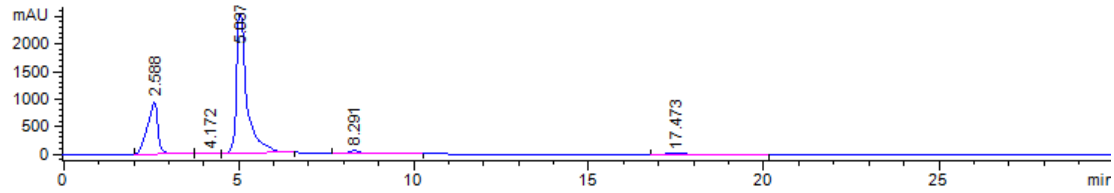
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.24 mg/ml.

(c) 190 °C, 1 h, 10.0 g EG, 0.2 g catalyst



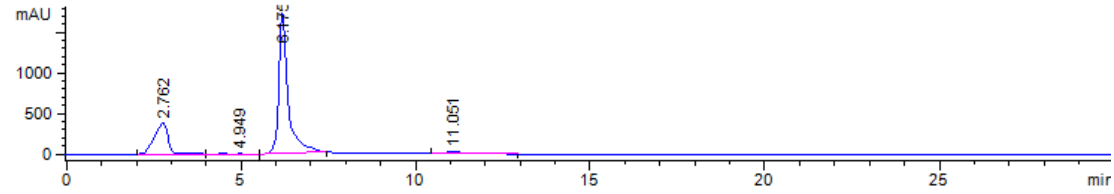
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 7.90 mg/ml.

(d) 195 °C, 1 h, 10.0 g EG, 0.2 g catalyst



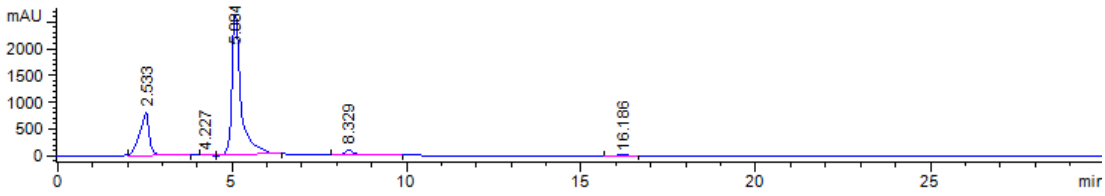
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 10.19 mg/ml.

(e) 185 °C, 0.5 h, 10.0 g EG, 0.2 g catalyst



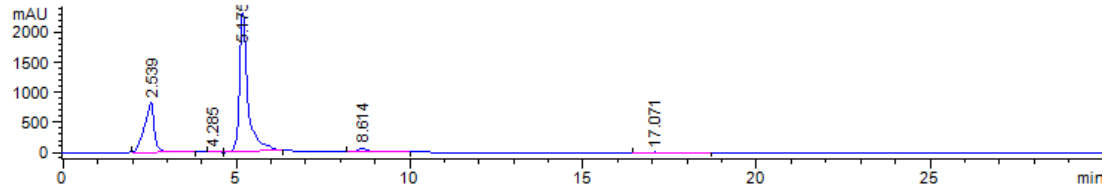
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.17 mg/ml.

(f) 185 °C, 2 h, 10.0 g EG, 0.2 g catalyst



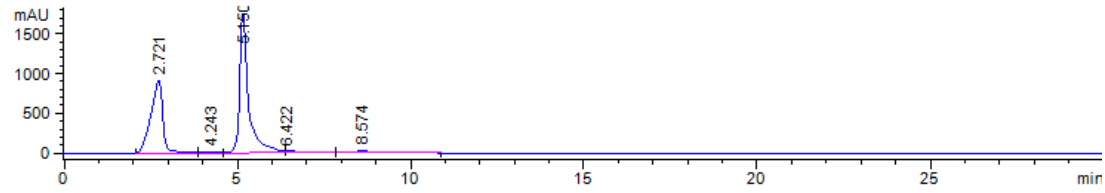
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 9.26 mg/ml.

(g) 185 °C, 3 h, 10.0 g EG, 0.2 g catalyst



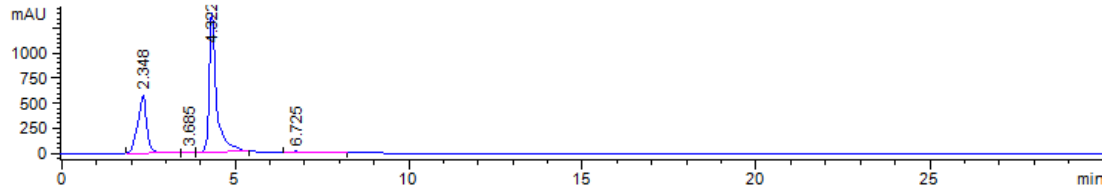
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 7.56 mg/ml.

(h) 185 °C, 1 h, 5.0 g EG, 0.2 g catalyst



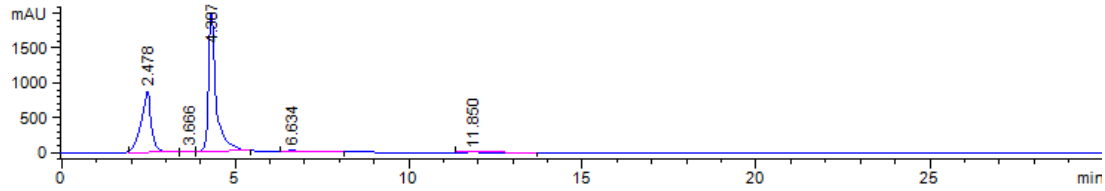
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.08 mg/ml.

(i) 185 °C, 1 h, 7.5 g EG, 0.2 g catalyst



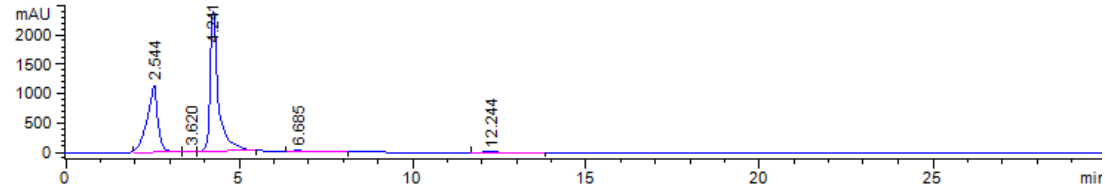
After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.93 mg/ml.

(j) 185 °C, 1 h, 10.0 g EG, 0.3 g catalyst



After filtering crystal monomer BHET, the content of BHET in reaction mixture is 6.91 mg/ml.

(k) 185 °C, 1 h, 10.0 g EG, 0.4 g catalyst



After filtering crystal monomer BHET, the content of BHET in reaction mixture is 7.55 mg/ml.

Ionic liquid and metal salts as catalysts for the glycolysis in the literature.

Source	Catalyst	Temperature (ºC)	Time (h)	PET:EG (mass)	PET:catalyst (mass)	C_{PET} (%)	S_{BHET} (%)	Y_{BHET} (%)
Qian Wang 2013[34]	$[C_1mim][ZnCl_3]$	175	1.25	5:20	5:0.5	100	80.1	80.1
	$[C_1mim][CoCl_3]$	175	1.25	5:20	5:0.5	100	79.5	79.5
Qun Feng Yue 2013[51]	$[C_4mim]Cl$	190	8	2:22	2:0.1	100	57.1	57.1
	$[C_4mim]ZnCl_3$	190	2	2:22	2:0.1	100	82.6	82.6
	$[C_4mim]ZnCl_3$	190	2	2:22	2:0.05	100	83.0	83.0
	$[C_4mim]ZnCl_3$	190	2	2:22	2:0.025	100	84.9	84.9
	$[C_4mim]ZnCl_3$	190	2	2:22	2:0.0126	100	83.4	83.4
	$[C_4mim]MnCl_3$	190	2	2:22	2:0.1	100	83.3	83.3
Qian Wang 2014[53]	$[C_4mim][MnCl_3]$	170	4	5:20	5:1	86.7	72.1	62.5
	$[C_4mim][FeCl_4]$	170	4	5:20	5:1	94.7	58.9	55.8
	$[C_4mim]_2[CoCl_4]$	175	1.5	3:35	3:0.5	100	81.1	81.1
	$[C_4mim]_2[NiCl_4]$	170	4	5:20	5:1	45	64.3	28.9
	$[C_4mim]_2[CuCl_4]$	170	4	5:20	5:1	6.7	9.8	0.7
	$[C_4mim]_2[ZnCl_4]$	170	4	5:20	5:1	99.6	77.4	77.1
Ahmed. Al-Sabagh 2014[54]	$[C_4mim][OAc]$	190	3	3:20	3:1	100	58.2	58.2
Hui Wang 2009[35]	$[C_4mim]H_2PO_4$	175	8	5:20	5:1	6.9		
	$[C_4mim]HSO_4$	170	8	5:20	5:1	0.5		
	$[C_4mim]Cl$	180	8	5:20	5:1	44.7		
	$[C_4mim]Br$	180	8	5:20	5:1	98.7		
	$[C_4mim]Cl$	190	8	5:20	5:4	100	> 60	> 60

Source	Catalyst	Temperature (°C)	Time (h)	PET:EG (mass)	PET:catalyst (mass)	C_{PET} (%)	S_{BHET} (%)	Y_{BHET} (%)
Qun Feng Yue 2011[50]	$[C_4mim]OH$	190	2	2:20	2:0.1	100	71.2	71.2
	$[C_4mim]HCO_3$	190	2	2:20	2:0.1	82.8	17.0	14.1
	$[C_4mim]Cl$	190	2	2:20	2:0.1	28.9	20.7	6.0
	$[C_4mim]Br$	190	2	2:20	2:0.1	10.7		
R.Lopez-Fonseca 2010[41]	$Zn(Ac)_2$	196	1	30:73.5	30:0.35			64.0
	Na_2SO_4	196	1	30:73.5	30:0.058			10.0
	K_2SO_4	196	1	30:73.5	30:0.071			1.0
R.Lopez-Fonseca 2010[32c]	Na_2CO_3	196	1	30:73.5	30:0.017			78.8
	$NaHCO_3$	196	1	30:73.5	30:0.07			60.2
Xi 2005[38]	$Zn(Ac)_2$	196	3	1:5	1:0.01			85.6
Troev 2003[40]	$Ti(PO_4)_4$	200	2.5		1:0.003			97.5
Navnath D. Pingale 2009[86]	$ZnCl_2$	197	8	1:10	1:0.005			74.7
	LiCl	197	8	1:6	1:0.005			63.1
	$MgCl_2$	197	8	1:6	1:0.005			65.6
	$FeCl_3/FeCl_2$	197	8	1:6	1:0.005			61.1